Volume 30 DECEMBER, 1960 Number 4

Journal of Sedimentary Petrology

A Publication of the Society of Economic Paleontologists and Mineralogists
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Relations of settling velocity of sand-sized spheres and sample weights. By Jessie D. Hulsey.

Early diagenetic dolomite associated with salt extraction process, Inagua, Bahamas. By D. N. Miller, Jr.

A simplified method for determining relative energies of deposition of stratigraphic units. By Glenn S. Visher.

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FIGS. 1–11, PLATES 1–3, DECEMBER, 1960

HEAVY MINERALS IN LOWER TERTIARY FORMATIONS IN THE SANTA CRUZ MOUNTAINS, CALIFORNIA[1]

ALEXANDER J. BEVERIDGE
Canberra Oil Company Ltd., Calgary, Alberta

ABSTRACT

A total of 38 heavy minerals were found in Butano (Eocene), San Lorenzo (Oligocene) and Vaqueros (Miocene) Formations in the Santa Cruz Mountains, but of these, only 13 occur in appreciable amounts. They are: apatite, biotite, chlorite, epidote, garnet, hematite, ilmenite, leucoxene-anatase, pyrite, rutile, sphene, tourmaline, and zircon.

Stratigraphic variations of heavy mineral frequencies in the Butano and Vaqueros Formations are significant through both vertical and horizontal intervals. The San Lorenzo Formation, however, is dominantly shale, and the percentages of heavy minerals therein are too low to allow detailed study. The mineral variations in the Butano and Vaqueros sands are attributed to four main processes: (1) differential sorting, (2) concentration of stable minerals by removal of unstable species, (3) diagenetic alteration, and (4) changes in intensity of erosion and weathering at the source plus changes in mode of transport to the site of deposition.

Diagenesis, which plays an important role in the alteration of ilmenite and sphene to leucoxene (or anatase), appears to have been more active in the northernmost sections of these formations, where increased distance from shore and source of sediments may have been a controlling factor in mineral alterations.

The main distributive province from which the heavy minerals of these lower Tertiary sedimentary rocks were derived is the area in which the Ben Lomond quartz diorite and adjacent metamorphic rocks occur. A secondary terrane which appears to have made a minor but significant contribution to early Tertiary sedimentation in this area is the pre-Tertiary (Franciscan) sedimentary, metamorphic, and basic igneous terrane northeast of the San Andreas fault.

INTRODUCTION

This study was undertaken primarily to determine the nature, distribution, and source of the heavy minerals which occur in lower Tertiary sedimentary rocks of the Santa Cruz Mountains, California. A secondary objective was the evaluation of the use of heavy mineral assemblages as a means of correlating these particular sedimentary formations throughout the local Tertiary basin.

LOCATION AND GENERAL GEOLOGY

The area under study occupies about 120 square miles in the Santa Cruz Mountains of the Coast Ranges of California from lat 37°00′N. to 37°30′N. and long 122°00′W. to 122°30′W. It is bounded on the northeast by the northwest trending San Andreas fault, on the west by the Pacific Ocean, and on the south by Ben Lomond Mountain (see fig. 1).

The Santa Cruz Quadrangle was first mapped for the U. S. Geological Survey by Branner, Newsom, and Arnold (1908) whose work appears in U. S. Geol. Survey Folio No. 163. The index map of this study (fig. 1) as well as the major structural features shown thereon have been taken from this folio.

Four major geologic features important to this study which are noted on the index map are: (1) Montara quartz diorite intrusive, the southern tip of which appears in the northwest part of the map area; (2) the northwest striking San Andreas fault and, more important, the band of pre-Tertiary sediments which occur immediately northeast of the fault; (3) the Tertiary sedimentary basin which occupies the central part of the map area; (4) Ben Lomond quartz diorite intrusive which bounds the area to the south. These are the features which form the source and site of deposition of the heavy minerals of the formations studied.

The Tertiary sedimentary basin appears to have been formed during late Cretaceous time, but the bulk of sedimentation within

[1] Manuscript received January 13, 1960.

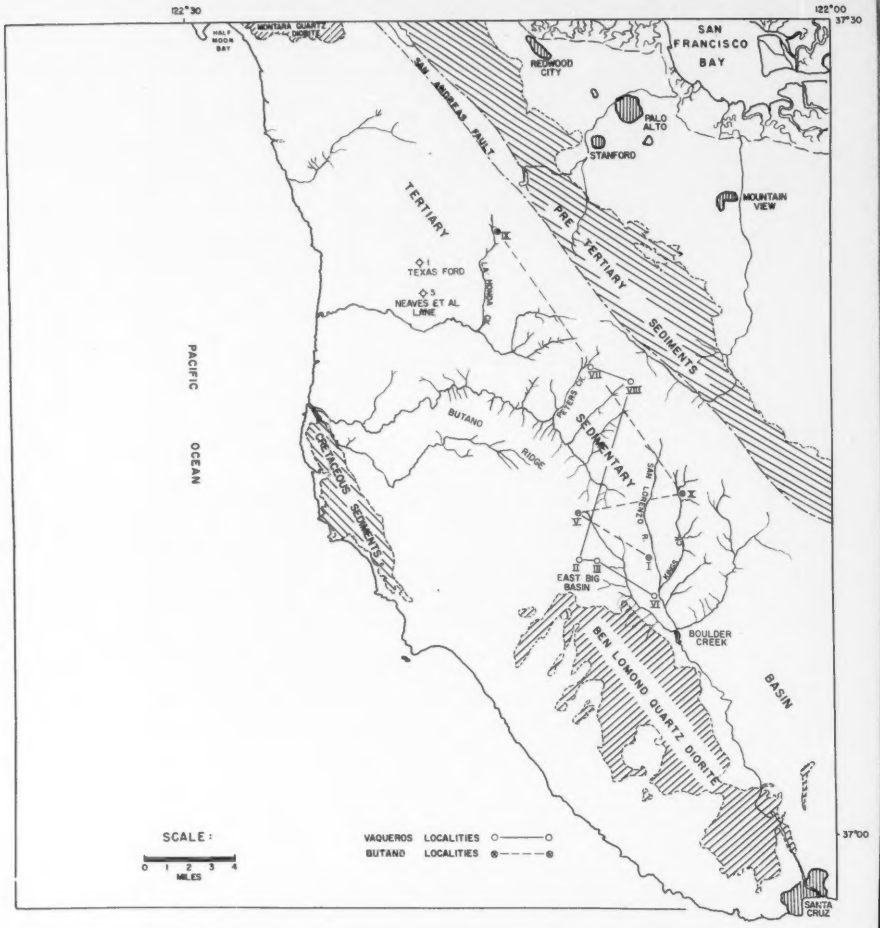

FIG. 1.—Santa Cruz Quadrangle showing principal geologic features.

the basin occurred throughout Tertiary time. The known strata range in age from Paleocene to Plio-Pleistocene with occasional depositional breaks throughout the section.

The formations studied here were deposited concordantly during early Tertiary time and are: Butano Sand of Eocene age, San Lorenzo Shale of Oligocene age, and Vaqueros Sand of Miocene age (see table 1). The Butano and San Lorenzo Formations are widespread throughout the basin, but the Vaqueros Formation is at a maximum development adjacent to Ben Lomond Mountain and pinches out a few miles north of Peters Creek, Locality VII (fig. 1).

The San Lorenzo Formation alone is completely exposed in the area; the other two units are only partially complete in any one exposure. For this reason, the Butano Sand

was studied immediately below and the Vaqueros, immediately above its contact with the San Lorenzo Formation. This facilitated lateral correlation of the units and enabled the use of paleontological control in the fossiliferous San Lorenzo Shale.

Because of insufficient vertical and lateral control of sands or siltstones in the San Lorenzo Formation, this unit has contributed very little to the interpretation of mineral variations. It was studied at only one locality (Wildwood, Loc. VI) near its upper contact with the Vaqueros Sand where eight thin sandstone lenses occur in a predominantly shale section.

SAMPLING

The exposures of Butano and Vaqueros Formations studied here were selected on the basis of maximum true thickness of sandstone in continuous sequence plus the presence of a known plane of reference, namely the lower or upper contact respectively of the San Lorenzo Formation.

Initially, spot samples 1 to 2 pounds in weight were collected in continuous linear series every 25 to 30 ft if the sands appeared homogeneous or at every change in lithology. Later, when it was found that vertical variation of mineral frequencies was not extreme, the sample interval over homogeneous sand sections was increased to 50 to 100 feet. Sample collection at lithologic breaks was maintained throughout the study.

A total of 130 surface samples and four Butano Formation core samples from two abandoned exploratory test wells were examined. These latter four samples of fresh rock were not used for correlation purposes but were extremely useful for determining the effect of weathering on surface samples.

The localities of all exposures sampled and studied and the exploratory well locations are shown on figure 1.

LITHOLOGY

The majority of rocks studied are very fine to medium grained sands (or sandstones), the primary constituents of which are quartz, chert, and feldspar (orthoclase, microcline, and oligoclase to andesine plagioclase). Minor constituents include biotite and volcanic material. In most cases the rocks are soft and coherent, but occasional specimens taken from adjacent concretionary structures are very hard, calcareous sandstones. The grains are angular to subangular except in the coarser grade sizes (.5 to 2.0 mm) where abrasion has more effectively rounded many of the grains.

No detailed examination was made of the sands in thin section; however, on the basis of field examination, grain mounts of the "light" fraction, and size analyses, most sands may be classed as feldspathic arenites

TABLE 1.—*Geologic formations in the Santa Cruz Mountains, California*

Period	Epoch	Formation	Thickness	Lithology
Tertiary	Plio Pleistocene	Santa Clara Fm.	500′	Fresh water gravels, sands, clays.
	Pliocene	Merced Fm.	100′	Shale and arkose.
	———	Purisima Fm.	2000′	Tuffaceous sandstone.
	Miocene	Monterey Fm.	1000′	Siliceous shale.
		Sandholt Fm.	2500′	Shale and siltstone.
		Vaqueros Fm.	0–2500′	Sandstone and shale.
	Oligocene	San Lorenzo Fm.	1800′	Shale and siltstone.
	Eocene	Butano Fm.	2500′	Sandstone and shale.
	Paleocene			

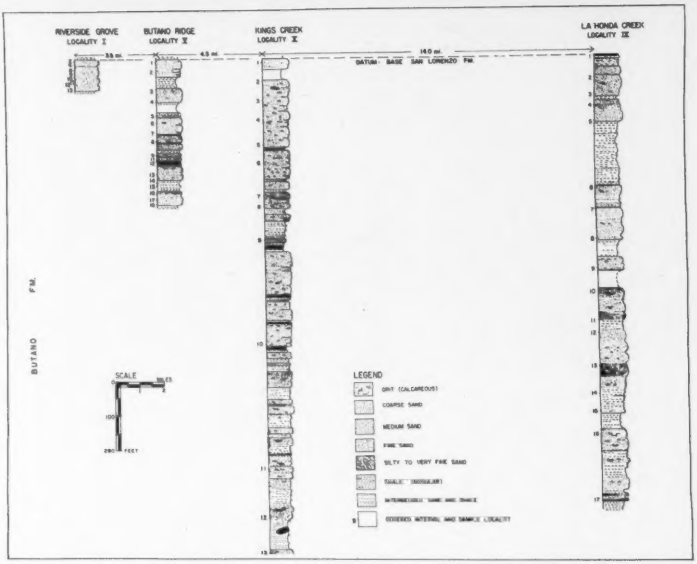

FIG. 2.—South-north stratigraphic section of Butano Formation showing sample localities.

(Williams, Turner, and Gilbert, 1955, p. 290).

Figures 2 and 3 are stratigraphic sections of the Butano and Vaqueros Formations respectively; the lower and upper contact of the San Lorenzo Formation is the datum in each section.

SAMPLE PREPARATION AND MINERAL SEPARATION

From a 100.0 gm fraction of completely disaggregated sand, particles less than .022 mm diameter were removed by standard elutriation methods. After drying, the sample was weighed and sieved (on a mechanical shaker) through a series of Tyler screens with openings: 2 (#9), 1 (#16), .5 (#32), .25 (#60), .125 (#115) and .062 (#250) mm; each resulting fraction was weighed and bottled.

The method of heavy mineral separation outlined by Hutton (1950, p. 641), namely, settling of heavy minerals in bromoform ($d=2.8$) in a steep sided evaporating dish followed by decantation of the "light" fraction, was used here for particle sizes larger than .062 mm diameter. For the silt-size material (less than .062 mm diameter), separation was effected by centrifuging in bromoform. After separation the heavy residue was washed in acetone, dried, and weighed. Ferromagnetic material was removed with an AC hand magnet, the weights recorded, and the remainder of the sample was split using an Otto microsplit before mounting in Canada balsam ($n=1.54$).

Only the three finest size fractions ($-60+115$, $-115+250$, and -250 mesh) were mounted, because grains larger than 60 mesh (.25 mm) generally exhibit abnormal optical properties. The material coarser than 60 mesh was examined under a binocular microscope, and grains which could not be identified immediately were separated, crushed to smaller size in a drop of clove oil ($n=1.54$) on a glass slide, and then identified optically.

Each mounted slide was examined thoroughly to ensure identification of all grains prior to counting and to take note of any minerals which, because of their rarity, may

not be included in the count. With a mechanical stage mounted on the microscope, a representative count of 400 grains per slide was made wherever possible.

SIZE ANALYSES

Size frequency curves for both Butano and Vaqueros Sands have been plotted in figures 4 and 5 in order to illustrate grain size variation and relative sorting of both light and heavy mineral fractions of the sands. For purposes of simplicity only two sections of each formation were chosen, one from the south, the other from the northern part of the area. Eight samples are shown for each section; four of these yielding the greatest weight of heavy minerals are plotted along the top line of each section from left to right in decreasing order of weight (V-11, V-14, V-15, and V-16, Butano Ridge, fig. 4); the other four samples which yield the least weight of heavy minerals are plotted immediately below the first four from left to right in increasing order of weight (V-5, V-6, V-8, and V-18, Butano Ridge, fig. 4). Absolute weights of heavy minerals per 100.0 gm of sand are also recorded for each sample. All other samples from these sections occupy an intermediate position between the two extremes.

In general, coarser grained and more poorly sorted Butano sands yield less heavy minerals than those of fine grain and better sorting; this applies to both Butano Ridge and La Honda Creek sections. Furthermore, a marked decrease in grain size and improvement of sorting occurs between the south section at Butano Ridge and the northern La Honda Creek section. This suggests a southern source of sediments. The increase in heavy mineral content from south to north on first appearance contradicts the theory of a southern source; most of the increase, however, can be attributed to the presence of authigenic pyrite and its alteration product, hematite. The bimodal character of some heavy mineral frequency curves at La Honda Creek is caused in all cases by the abundance of pyrite or hematite in the coarser grade sizes. The heavy mineral peak between .50 and .25 mm diameters at Butano Ridge (V-11) is caused

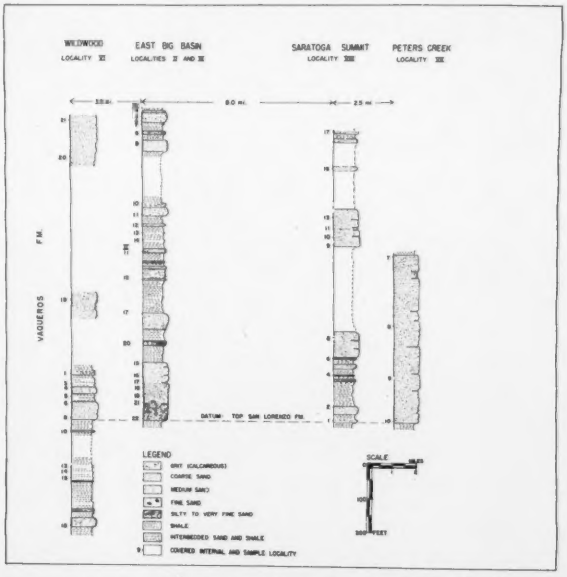

FIG. 3.—South-north stratigraphic section of Vaqueros Formation showing sample localities.

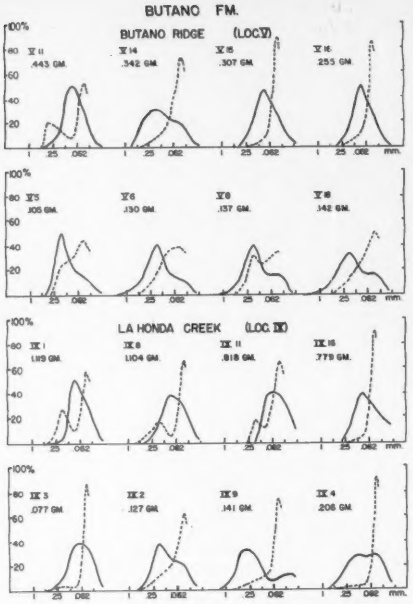

FIG. 4. Frequency curves of sands from Butano Formation. Solid line—total sand; dotted line—heavy minerals only. Weight shown is total weight of heavy minerals per 100 gm of sand.

by composite particles of leucoxene, quartz, and feldspar.

Vaqueros sands from East Big Basin (Loc. III) and Saratoga Summit (Loc. VIII, fig. 5) are generally coarser grained and more poorly sorted than those of the Butano Formation, but unlike the Butano, there appears to be no distinct correlation between sorting and heavy mineral yield. There is an increase in yield with decrease in grain size, however, which is particularly noticeable between samples of maximum and minimum yield at the same locality (III-7 and III-21; VIII-11 and VIII-2, fig. 5). The bimodal character of some Saratoga Summit heavy mineral curves is caused entirely by sphene and leucoxene in the coarser fractions of these sands. This suggests that increase of leucoxene with increasing grain size is caused principally by the original coarse grain size of parent sphene and ilmenite grains. This relationship is discussed more fully in a later section.

The heavy mineral yield decreases from south to north between East Big Basin and Saratoga Summit, but no change in grain size or sorting of the sands is apparent. This decrease, together with the rapid formational thinning to the north, suggests again a southern source for these sediments. The lack of uniform decrease in grain size and lack of sorting, however, indicate conditions of transport and deposition differed greatly from those during Butano sedimentation.

The Vaqueros Formation at its southernmost locality (East Big Basin) yields more heavy minerals than the Butano Formation at its southernmost locality (Butano Ridge). This is probably a function of relative distance from source, degree of weathering and erosion at the source, and intensity of post-depositional solution.

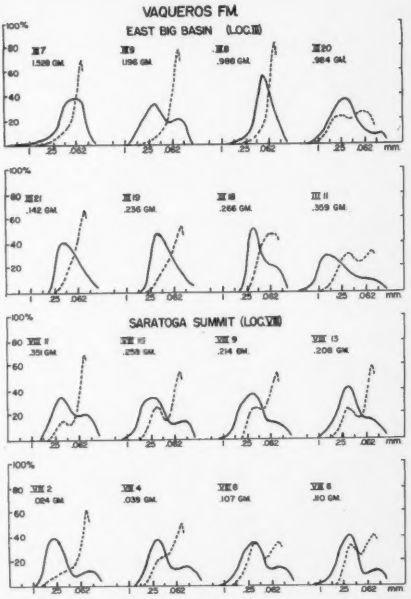

FIG. 5. Frequency curves of sands from Vaqueros Formation. Solid line—total sand; dotted line—heavy minerals only. Weight shown is total weight of heavy minerals per 100 gm of sand.

In samples studied here, the greatest heavy mineral yield as well as the greatest diversity of mineral species occurs in the silt size fraction (−250 mesh). Many studies in the past have been concerned only with heavy minerals in grade sizes coarser than 200 or 250 mesh, with the result that much of the data are incomplete. This is unfortunate because conclusions regarding source and diagenesis based on these incomplete data may be erroneous. Cogen (1935) proposed a method of investigating heavy minerals in sediments whereby one grade size only is used for mineral identification and comparison with those in rocks from different areas. This method is also incomplete, especially with respect to stratigraphic variation of mineral frequencies with different grade sizes, and unless all size fractions are examined, there is a good possibility that many diagnostic minerals may not be identified.

MINERALOGY

A total of 38 heavy minerals were found in sands of the Butano, San Lorenzo, and Vaqueros Formations, but of these, only 13 occur in appreciable amounts. These more common minerals are described below.

Apatite

Apatite is common to abundant in the fine grade sizes of Butano, San Lorenzo, and Vaqueros sands and siltstones. The vertical (stratigraphic) distribution of this mineral is quite irregular since the heavy fraction of some samples is dominantly apatite, whereas in other instances a few hundred feet above or below, apatite is lacking.

It occurs in rounded, anhedral grains and euhedral prisms (pl. 1, figs. 14, 15) that range in ratio of length:breadth from 1:1 to rarely 10:1; most are approximately 2:1.

In general, apatite is fresh and unaltered, but many grains exhibit a well-developed "cockscomb" structure, a form of corrosion which, judging by its apparent fragility, was caused by either post-depositional solution or surface weathering (Smithson, 1942). It is usually colorless, but abundant dust-like inclusions commonly impart a gray or smoky coloration to the grains. Dichroism is a rare to occasional property of apatite from Butano and Vaqueros sands; the usual scheme is E = colorless, pale pink; O = brown, bluish gray, deep violet. Some otherwise colorless grains contain elongate, dichroic cores (pl. 2, fig. 15).

Inclusions are generally numerous but aside from the more common cavities and black, opaque dust, the more notable mineral inclusion is amphibole.

Biotite

Biotite is abundant and widespread in all grade sizes of these lower Tertiary sands. It is usually more abundant in the grade sizes coarser than 250 mesh, although in the Butano Formation at Kings Creek (Loc. X) and La Honda Creek (Loc. IX) it is more common in the finest grade size (−250 mesh). This phenomenon appears to be related to the much finer texture of the sandstones and siltstones at these localities.

Biotite occurs usually as irregular, basal flakes although well-developed pseudo-hexagonal outlines are not uncommon. Gradations in composition from the phlogopite end through siderophyllite are present; the low-iron variety is concentrated along with the "light" minerals, while iron-rich varieties separate with other heavy minerals. Color is usually pale sepia brown to dark reddish brown, but in the Butano Formation of Riverside Grove (Loc. I) and Butano Ridge (Loc. V), a bright reddish orange biotite was observed occasionally. This latter variety has $nY = 1.65$; $2Vx = 40°$; $r < v$ very strong. It was noted by Hutton (1952) in some California beach sands and is very similar to titaniferous phlogopite described by Prider (1939).

Chlorite

Chlorite is a widespread, generally minor constituent in all size fractions of these sands. It occurs most abundantly in the −250 mesh grade size of Butano sands at Kings Creek (Loc. X) and La Honda Creek (Loc. IX), where its frequency, like that of biotite, bears a direct relationship to argillaceous content and an inverse relationship to grain size of the rocks.

It occurs usually in the form of olive and brownish green, basal flakes which may be irregular to almost hexagonal in outline.

The association of chlorite with biotite in very fine grained sedimentary rocks and the

PLATE 1.—Heavy minerals from the Butano Formation, Riverside Grove.

presence of sagenitic networks of ilmenite in many chlorite grains suggest strongly that much of the chlorite has formed from biotite. The titanium content of biotite is rejected during alteration of mica to chlorite and now appears as sagenitic networks of ilmenite. Alteration does not appear to have taken place in the sediments because both chlorite and biotite are fresh and mineral flakes in transition are extremely rare. Alteration may have occurred at the source.

Epidote

Epidote is an abundant mineral in Butano and Vaqueros sands, particularly so in the latter, and all gradations from iron-rich (pistacite) to iron-poor (clinozoisite) epidote are found. It is the predominant mineral of the finest grade size of some Vaqueros sands at Saratoga Summit (Loc. VIII) and East Big Basin (Loc. III), but decreases only slightly in abundance in the $-115+250$ mesh size fraction. Epidote from sands of the Butano Formation is generally more abundant in the $-115+250$ mesh fraction but, as in the Vaqueros, it is present in all grade sizes.

Angular, equidimensional anhedra predominate, but variable degrees of rounding are found; in one sample of Butano sand at Kings Creek (Loc. X) exceptionally elongate euhedra with ratio of length:breadth = 5:1 were observed.

Corrosion, in the form of "cockscomb" terminations, is very pronounced in some samples (see pl. 3, figs. 5, 7, 8), and here and there surface etching that superficially resembles "microscaly" garnet etching is to be seen.

Garnet

At least two varieties of garnet are present in the Tertiary sands. The most abundant is grossularite which usually comprises 80 to 90 percent of total garnet; the other is pink to deep red spessartite-almandine. This pink variety, although subordinate in abundance to grossularite in the fine size fractions, is invariably the principal garnet in the +60 mesh and coarser grade sizes. A very rare orange garnet was noted, but owing to its scarcity no data were obtained.

Usually both grossularite and spessartite-almandine occur as angular, equant grains although frequently dodecahedral faces and forms were noted. Some pink grains are very well rounded and near-spherical, but the majority of both colorless and pink garnet grains are angular to subangular. Surface etching is a common feature of these garnets, but unlike the rectangular-appearing

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EXPLANATION OF PLATE 1

FIG. 1.—Zircon, elongate, euhedral, showing inclusions and cavities.
FIG. 2.—Zircon, euhedral with overgrowth on terminal.
FIG. 3.—Zircon, "double" crystal.
FIG. 4.—Zircon, rounded and elongate showing surface pits.
FIG. 5.—Zircon, euhedral with elongate central cavities.
FIG. 6.—Zircon, elongate, euhedral.
FIG. 7.—Hyacinth zircon, rounded.
FIG. 8.—Zircon showing (111) cleavages.
FIG. 9.—Tourmaline, well rounded, containing inclusions.
FIG. 10.—Tourmaline, well rounded.
FIG. 11.—Apatite, etched, showing incipient corrosion parallel to *c*-axis.
FIG. 12.—Rutile, rounded with striations parallel to *c*-axis.
FIG. 13.—Apatite, corroded, showing "cockscomb" terminals.
FIG. 14.—Apatite, euhedral, containing zircon inclusion and cavities.
FIG. 15.—Apatite, elongate, euhedral.
FIG. 16.—Tourmaline, euhedral, containing fine dust-like inclusions.
FIG. 17.—Tourmaline, euhedral, containing dark inner core and light colored overgrowth.
FIG. 18.—Brookite, finely striated.
FIG. 19.—Monazite, rounded with black opaque inclusion.
FIG. 20.—Zircon, euhedral.
FIG. 21.—Anatase, euhedral basal section.
FIG. 22.—Monazite, rounded.

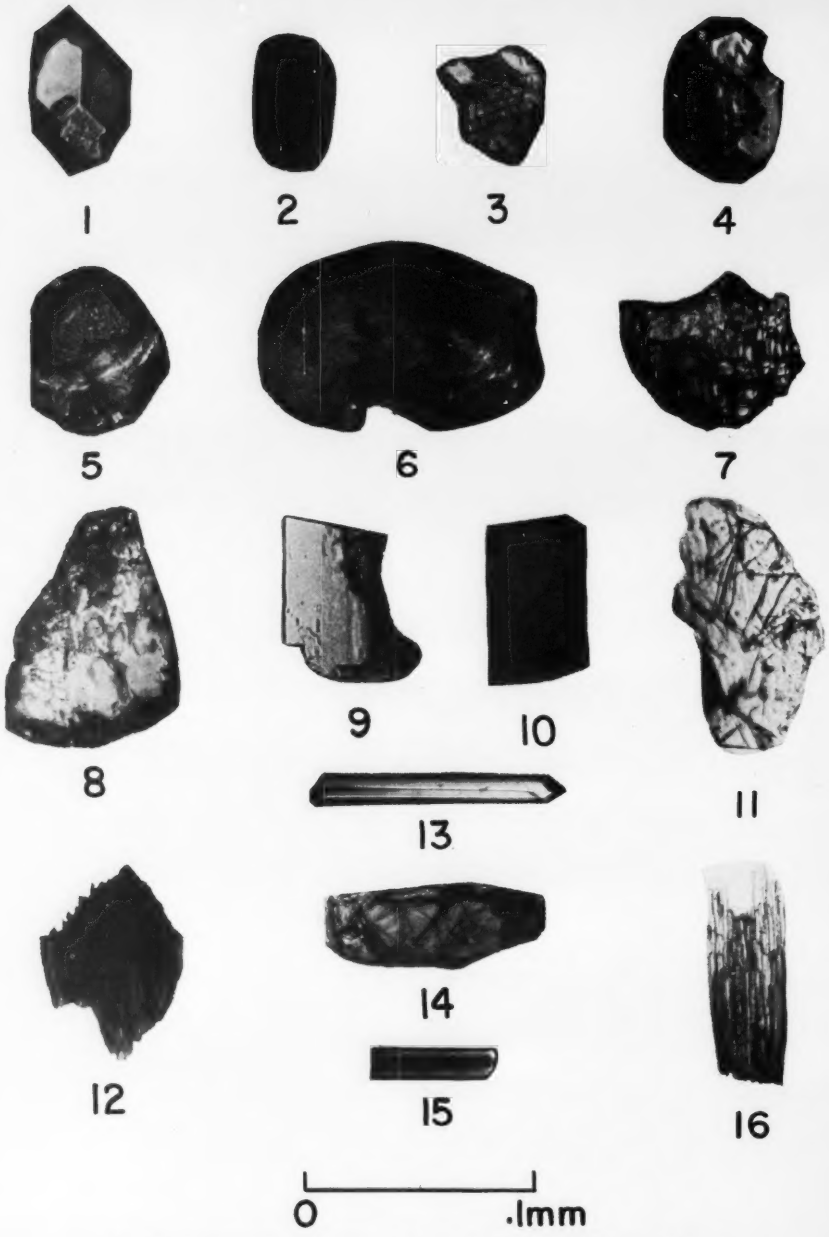

PLATE 2.—Heavy minerals from the Vaqueros Formation, East Big Basin.

depressions described by Bramlette (1929), the surface is marked by numerous elliptical pits which impart a "microscaly" appearance to the garnet.

Hematite

Hematite is ubiquitous in these sands and ranges from less than 1 percent to more than 90 percent of total heavy minerals. It occurs in all grade sizes; in fractions coarser than 60 mesh, it is generally found in aggregate grains cementing quartz, feldspar, and various heavy minerals.

Hematite occurs as irregular, but more often as spherical and botryoidal, grains of deep red, powdery agregates that are translucent at the thinnest edges only. Rarely, the mineral may pseudomorph magnetite octahedra or foraminiferal shell material; the latter case probably represents multiple stage replacement of the original aragonite or calcite by pyrite which has later oxidized to hematite.

Ilmenite

Ilmenite, abundant and widespread in these lower Tertiary sands, is particularly so in the southernmost localities where it usually comprises 20 to 30 percent, with local increases to more than 50 percent, of the heavy minerals. It is common in all fractions, but becomes less abundant in those grade sizes coarser than 115 mesh.

Ilmenite is mostly black, occasionally tarnished to purplish blue, with good metallic luster. The grain surfaces, unlike magnetite and chromite, are frequently rough and pitted except on shiny conchoidal fracture surfaces. It occurs most commonly as anhedral grains and fragments, but platy and tabular subhedra showing base and rhombohedron were observed in a few samples. Shape and degree of rounding are variable and range from well rounded, ellipsoidal grains to angular plates and more or less equidimensional fragments. Most of the grains are exceedingly fresh, although occasional surface coatings of pale brown to creamy white leucoxene and deep red hematite do occur.

Occasionally, very thin splinters are translucent with the deep brown color of geikelite, but in most instances ilmenite is quite opaque.

Leucoxene-Anatase

Leucoxene, the most abundant and widespread heavy mineral in these sands, comprises up to 90 percent of the heavy minerals in many samples. In the finest fraction, it occurs as white, creamy, and pink porcellaneous grains and clumps of fine powdery material; in size fractions coarser than 60 mesh, it occurs usually in aggregate grains of quartz, hematite, and other heavy minerals.

It is the alteration product of both ilmenite and sphene, but apart from occasional surface coatings of leucoxene on ilmenite, the alteration of the latter is not obvious. Sphene, on the other hand, shows all gradations from fresh, unaltered particles to those

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EXPLANATION OF PLATE 2

FIG. 1.—Zircon, euhedral.
FIG. 2.—Rutile, rounded.
FIG. 3.—Sphene, slightly rounded and showing "rhombic" cracks.
FIG. 4.—Sphene, euhedral, containing central core of rounded sphene.
FIG. 5.—Sphene, euhedral.
FIG. 6.—Sphene, rounded with faint surface coating of leucoxene.
FIG. 7.—Sphene, etched in "rhombic" pattern.
FIG. 8.—Sphene fragment.
FIG. 9.—Clinozoisite, broken, euhedral.
FIG. 10.—Tourmaline, euhedral, showing numerous fine cracks.
FIG. 11.—Muscovite, containing many acicular amphibole inclusions.
FIG. 12.—Augite, corroded.
FIG. 13.—Zircon, elongate, euhedral.
FIG. 14.—Zoisite with golden brown stain.
FIG. 15.—Apatite, euhedral with elongate pleochroic core.
FIG. 16.—Actinolite, corroded.

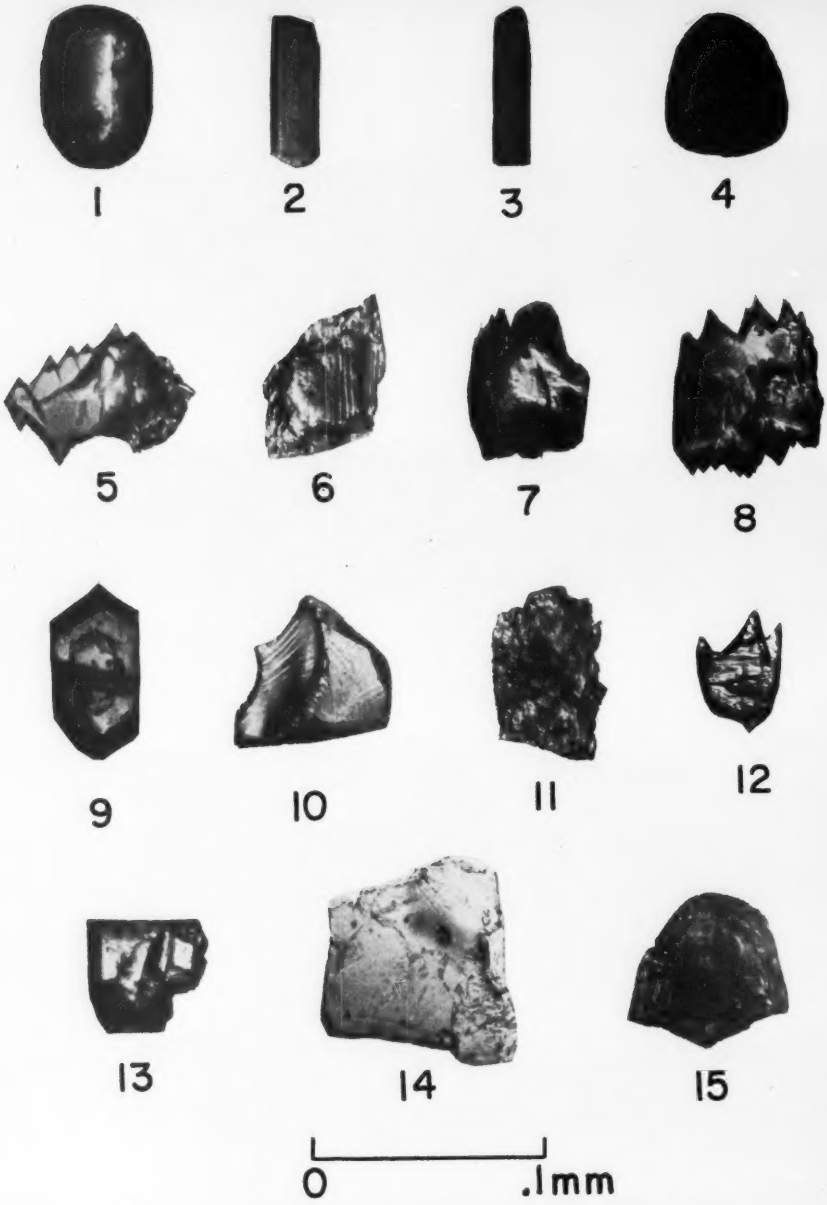

PLATE 3.—Heavy minerals from the Butano Formation, Butano Ridge.

that are 90 percent leucoxene. Many grains from sands of northern localities retain only a small central core of relatively unaltered sphene, whereas the remainder of the grain is white, opaque leucoxene. Most very light colored leucoxene has probably formed from sphene; material of pinkish and brownish cast is a likely derivative of ilmenite.

Sands of the Butano Formation at Kings Creek (Loc. X) and sands of the Vaqueros Formation at Saratoga Summit (Loc. VIII) contain particles showing complete gradation from cryptocrystalline and powdery leucoxene to creamy aggregates of minute, disoriented anatase tablets. Individual tablets are more or less equidimensional in each aggregate, but a pronounced gradation in size occurs between tablets of one aggregate grain and those of another. This suggests strongly that light colored leucoxene in these sands is merely cryptocrystalline anatase rather than any of the other titanium dioxide isomorphs (Coil, 1933; Tyler and Marsden, 1938).

Pyrite

The amounts of pyrite range widely. In medium to coarse sands with very little shaly material, pyrite is present in trace amounts only; in siltstones and some fine-grained sands, where shaly content exceeds 10 percent by weight of the rock, pyrite is the predominant heavy mineral. This association of pyrite with fine grained clastics is not only related to the environment of deposition but also to the permeability of the rock. Accessibility to oxidizing solutions (either diagenetic or weathering) is greatly reduced where much clay material has filled the interstices between sand grains; this results in preservation of pyrite. The pyritiferous, very fine grained sands of the Butano Formation at La Honda Creek (Loc. IX) illustrate very well this relationship between clay content and pyrite preservation. Where permeability of the rock is such as to allow widespread circulation of oxidizing solutions, pyrite is one of the first minerals to be altered.

Pyrite occurs most commonly as aggregates of very fine to microcrystalline material which is brassy yellow when fresh and red when tarnished or weathered. All degrees in alteration to hematite were observed in these samples.

Rutile

Rutile is a widespread but minor constituent of these Tertiary sands. It is restricted to the three finest size fractions and only rarely does it exceed 2 percent of the total heavy minerals in any one grade size.

Three distinct color varieties of rutile noted in these samples are (1) yellow, (2) wine red, and (3) chocolate brown. All varieties exhibit a range of dichroism to varying degrees, and types 2 and 3 show much more absorption than type 1.

Short, stumpy, subhedral grains predominate, but many dark chocolate brown and wine red euhedra have length:breadth ratios in excess of 3:1 (pl. 3, fig. 3). On the other hand, many rutile grains are subrounded to very well rounded (pl. 3, fig. 4).

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EXPLANATION OF PLATE 3

FIG. 1.—Hyacinth zircon, rounded.
FIG. 2.—Tourmaline, euhedral.
FIG. 3.—Rutile, elongate, subhedral.
FIG. 4.—Rutile, well rounded.
FIG. 5.—Clinozoisite, corroded.
FIG. 6.—Zoisite, showing perfect (001) cleavage.
FIG. 7.—Epidote, corroded.
FIG. 8.—Epidote, corroded.
FIG. 9.—Zircon, euhedral, containing euhedral zircon core.
FIG. 10.—Garnet fragment showing conchoidal fracture.
FIG. 11.—Garnet, etched and stained.
FIG. 12.—Zircon, corroded?
FIG. 13.—Anatase, euhedral.
FIG. 14.—Muscovite with pleochroic halo surrounding zircon inclusion.
FIG. 15.—Tourmaline showing concentric fissures.

Sphene

Sphene is very abundant in all sands studied from the Vaqueros Formation with the exception of those from the northernmost locality at Peters Creek (Loc. VII). It is very rare in the uppermost part of the Butano Formation but increases significantly in abundance in the lower part of the Butano sections studied; it is abundant in all Butano Formation core samples from N/C/U Lane #1. The frequency variations of this mineral are discussed more thoroughly under the section entitled "Stratigraphic Variation."

Sphene is usually colorless, pale yellow, or rarely pink in the finer grade sizes; with increase in grain size the colors become deeper and vary from golden yellow, or pale brown to rarely deep reddish brown. Most sphene occurs as equidimensional cleavage and fracture fragments which are angular in the finest grade size but become progressively more rounded with increase in grain diameter (pl. 2, fig. 6).

"Envelope" tablets are distinct from normal cleavage fragments by their very pale colors, extreme dispersion, general lack of inclusions or alteration products, and very smooth surfaces. Fragmentary grains are frequently pitted and cracked, and in many instances a pseudo-rhombic pattern of etching or incipient cleavage was noted (pl. 2, fig. 7). Rarely, two sets of striations or cleavages are developed which form a series of minute parallelograms on grain surfaces; this feature may represent the initial stages of the pseudo-rhombic etching which characterizes so many grains.

Corrosion and alteration of sphene are pronounced in the northern exposures of both Butano and Vaqueros sands. Corrosion is evident by the presence of grains showing "cockscomb" terminations and alteration by peripheral and patchy zones of white to creamy leucoxene. All stages of alteration occur from sphene grains with faint leucoxene spots to leucoxene masses containing small central cores of sphene.

Inclusions are common in many sphene grains and include black, opaque rods and irregular masses, clear, rod-shaped apatite, zircon, and variously shaped cavities. Zonal or secondary growth was noted in a few grains where a central core of slightly rounded sphene is surrounded by sphene of much paler color (pl. 2, fig. 4). The interface between central core and peripheral zone is usually sharp and clear with very little dusty included material.

Tourmaline

Tourmaline, ubiquitous but minor in all grade sizes of Butano, San Lorenzo, and Vaqueros sands, is extremely variable in habit, although subhedral and euhedral grains usually predominate. Trigonal prisms which range from short to long (length :breadth ratio = 4:1) are the forms most commonly observed; rhombohedral and pyramidal faces are also common, but rounding tends to obliterate these terminal faces. Forms are distinguished most readily in oblique illumination where reflection from the various faces aids in their identification.

The degree of rounding ranges from angular to very well rounded; short prisms tend to become nearly spherical when subjected to extreme abrasion in the course of reworking, but most grains are subangular suggesting perhaps only one cycle of sedimentation.

Four distinct color varieties, brown, blue, green, and pink, have been distinguished in these samples. Brown tourmaline is by far the most abundant, but all varieties show a very wide range of colors.

Inclusions are common in most tourmaline grains, but many pale colored forms are inclusion-free. The most common inclusion is black, opaque material which may be in the form of irregular masses, elongate rods, or dust (pl. 1, fig. 16). Zircon, tourmaline, and acicular needles (amphibole?) were noted in some grains; rarely the needles are arranged radially from a common center. Spherical and elongate cavities are so numerous in some cases that such grains appear quite cavernous.

Zircon

Zircon is abundant in all of these lower Tertiary sands. It is characteristically more abundant in the finest grade size and decreases notably in frequency in those fractions coarser than 115 mesh; it is very rare in the $-32+60$ mesh grade size and absent from the $-16+32$ mesh fraction. Rounding is another feature which shows variation with progressive increase in grain size. Most

particles in the −250 mesh fraction are euhedral with very little evidence of abrasion; those in the −115+250 mesh fraction, although still predominantly euhedral, show more rounding of the terminals; zircon grains in the −60+115 mesh fraction, in addition to being rare, are invariably rounded to subrounded. Most of this progressive rounding may be associated with a single cycle of transport and deposition; on the other hand, well-rounded grains which occur in the −115+250 and −250 mesh grade sizes in all probability are evidence of more than one cycle of sedimentation.

Two varieties of zircon are distinguished in these sands, namely, (1) colorless and (2) hyacinth. The colorless variety may comprise up to 70 percent of the heavy minerals in the −250 mesh grade size, but hyacinth is usually restricted to less than 3 percent of this fraction.

Colorless zircon.—This variety is predominantly euhedral with combinations of prisms and multi-order pyramids developed most frequently. Secondary outgrowths developed on the terminals were observed rarely (pl. 1, fig. 2) but none were noted growing from the prism face. No complete crystal elongation studies were made here, but in general those forms with length: breadth ratios of 2:1 or less predominate; this is in agreement with Poldervaart's (1955) study of sedimentary zircons. Many crystals have a ratio in excess of 6:1 (pl. 1, fig. 6), and many others, although shorter, are obviously fractured grains and may have been much longer at one time.

Distinct zoning is a rare feature in colorless zircon; however, very fine concentric bands which are concentrated near the periphery of the crystal appear to represent a form of zoning (Hutton, 1950, p. 688). Many euhedral zircons contain cores of euhedral zircon (pl. 3, fig. 9), well rounded hyacinth, and occasionally round opaque (malacon?) grains. This may be a form of zoning in the case of the euhedral zircon cores, but where the cores are hyacinth or malacon, the peripheral material is probably a much later generation and is considered to be a secondary overgrowth.

Hyacinth zircon.—The term "hyacinth" is applied to all zircon which ranges in color from very pale shades of pink to deep hyacinth or purple. Dark reddish brown malacon was observed in a few samples, but because this variety represents merely a further step in the process of metamictization of zircon (Tomita, 1954), it is considered with hyacinth.

Hyacinth is usually well rounded (pl. 1, fig. 7; pl. 3, fig. 1), but many grains, particularly in the finest fraction, are subangular and even euhedral. Crystal form, where developed, is generally similar to that of colorless zircon, especially the more simple prisms and pyramids; second and third order pyramids were not observed on any hyacinth crystals. Elongate (length: breadth ratio greater than 3:1), prismatic hyacinths are extremely rare in these samples, a fact which is in accord with their history. Throughout the course of recycling, long hyacinth crystals would be unable to survive as such and would be broken down into smaller fragments which, when rounded, would give no clue as to the original form.

Concentric zoning is very common in hyacinth and may extend the full width of the grain or it may be concentrated near the periphery. Many grains contain deep brown to black, opaque central cores from which many irregular fissures radiate.

The surfaces of some well-rounded hyacinth grains are minutely pitted and etched and resemble frosted quartz grains; this is probably a type of solution etching.

Minor Minerals

Other heavy minerals were noted in these lower Tertiary sands but because of their scarcity and generally normal properties, no detailed descriptions are presented. Because some of these minerals enter later discussions regarding provenance and authigenesis, they are listed here: actinolite, allanite, augite, barite, brookite, cassiterite, cerussite, chloritoid, chromite, diopside, dolomite, gahnite, galena, glaucophane, hornblende, hypersthene, magnetite, monazite, muscovite, pigeonite, siderite, spinel, staurolite, vesuvianite, and zoisite.

STRATIGRAPHIC VARIATION OF MINERAL FREQUENCIES

Figures 6 through 11 illustrate the variations in frequency of seven major mineral types from Butano and Vaqueros sands in

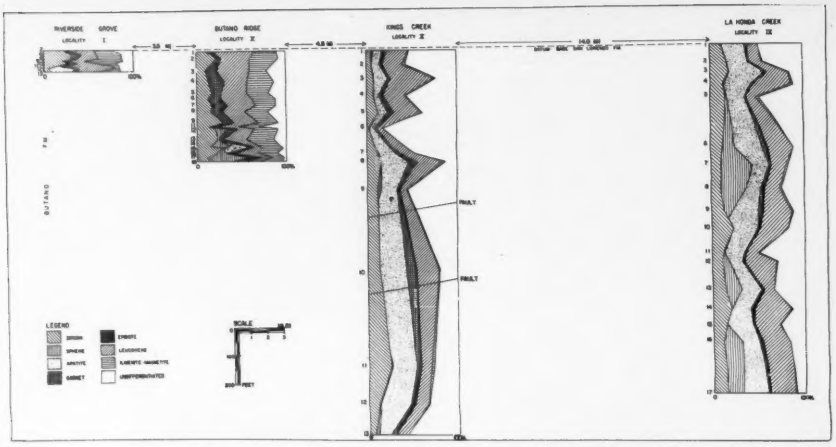

FIG. 6.—Stratigraphic variation of heavy mineral frequencies within the Butano Formation; screen size: −250 mesh.

vertical and horizontal plane. A column was prepared for each measured section; in the case of the Butano Formation, the ordinate represents formation thickness below the base of the San Lorenzo Formation; for Vaqueros sections, the ordinate represents thickness above the top of the San Lorenzo Formation. In all cases the abscissa represents cumulative mineral percentages by volume. Sections of the same formation were combined to illustrate lateral as well as vertical variation.

In the first case, consider figures 6 through 8, which illustrate stratigraphic variation in mineral frequencies for the three finest size fractions of the Butano Formation. Figure 6 illustrates the variations in the −250 mesh fraction, and because of the greater abundance of heavy minerals in this fraction, a more accurate picture of these variations may be obtained.

Pyrite and its alteration product, hematite, comprise most of the undifferentiated material shown at Kings Creek and La Honda Creek. Most, if not all, of this pyrite is authigenic and as such may be ignored in the analysis of detrital mineral variation. Leucoxene is also dominantly authigenic, but unlike pyrite it has formed from detrital minerals and hence plays an important role in the study of mineral variation.

In figure 6 zircon, garnet, leucoxene, and ilmenite maintain fairly uniform frequencies throughout the vertical extent of individual columns. Apatite frequencies are very regular at Kings Creek and La Honda Creek but are more erratic at Riverside Grove and Butano Ridge; the mineral is present only in the basal part of these latter sections. Sphene is a rare to minor constituent in the upper 300 ft of the Butano Formation. It increases in abundance below this depth, but is very erratic in distribution. Epidote appears and disappears throughout these sections but is never more than a minor constituent.

The antipathetic relationship between sphene and leucoxene is apparent in the basal part of the Butano Ridge section and locally in the La Honda Creek section; leucoxene decreases considerably in sphene-rich samples and increases abruptly in samples containing little or no sphene. The same relationship exists between ilmenite and leucoxene and is illustrated in the Riverside Grove section. This antipathetic relationship is in accord with observed alterations of sphene and ilmenite to leucoxene (anatase), and in this case is probably caused by both alteration at the source (Spotts, J. H., 1958, personal communication) and diagenetic alteration. Boswell

(1924) and Smithson (1941) observed the same relationship between these minerals in some Mesozoic rocks in England, which they attributed mainly to authigenesis.

Two major lateral changes in mineralogy occur in the −250 mesh size fraction of these Butano sections. Ilmenite is a major, persistent mineral at Riverside Grove and Butano Ridge, but in the interval between Butano Ridge and Kings Creek, a distance of 4.5 miles, this mineral decreases to 2 percent of the heavy minerals and remains a minor constituent in the 14-mile interval between Kings Creek and La Honda Creek. Leucoxene does not increase in these two ilmenite-poor sections; therefore, it is assumed that the disappearance of ilmenite is a function of sorting rather than alteration. Ilmenite, with a density of 4.7 gms/cm^3, is one of the heaviest minerals in this group, and would tend to settle first.

Apatite is much more abundant in the −250 mesh fraction at Kings Creek and La Honda Creek than it is at Riverside Grove and Butano Ridge. This also appears to be a phenomenon of sorting, controlled by the relatively low density (3.18 gms/cm^3) of apatite; this mineral would tend to settle out later than any other major heavy mineral with the exception of biotite. This theory is supported by the abundance of apatite in finer grained sediments at La Honda Creek, which indicates desposition further from shore compared to the coarser, near-shore sediments at Butano Ridge.

Another factor which may be partially responsible for the amount of apatite in finer grained sediments is the abundance of interstitial clay in the very fine sandstones and siltstones compared to the coarser sands at Butano Ridge. This clay would tend to reduce rock permeability, thereby restricting circulation of solutions capable of dissolving apatite.

Garnet shows a lateral decrease in abundance between Butano Ridge and La Honda Creek which, as in the case of apatite and ilmenite, is probably a result of progressive sorting.

Figure 7 illustrates mineral variations in the −115+250 mesh fraction of the Butano Formation and is similar in many ways to figure 6. Apatite is distinctly less abundant, however, than in the −250 mesh fraction; the zircon content decreases at Riverside Grove and Butano Ridge but increases sharply at Kings Creek and La Honda Creek; leucoxene and ilmenite frequencies increase generally over those in the finer fraction, and sphene, epidote, and garnet show no consistent changes.

The most notable anomaly in figure 7 is

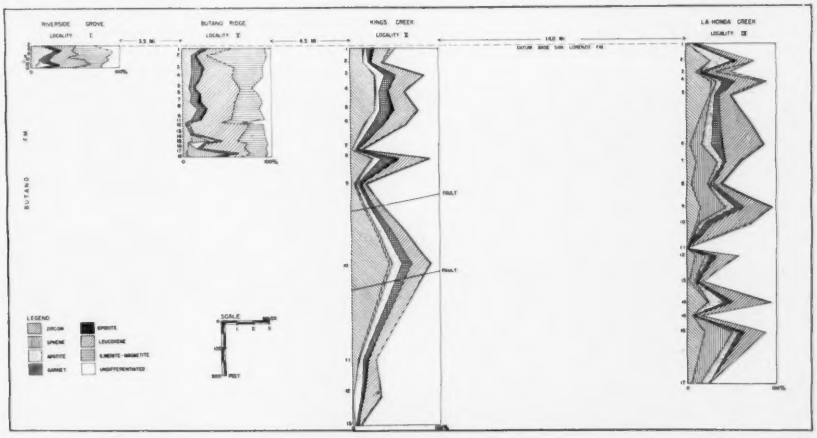

FIG. 7.—Stratigraphic variation of heavy mineral frequencies within Butano Formation; screen size: −115+250 mesh.

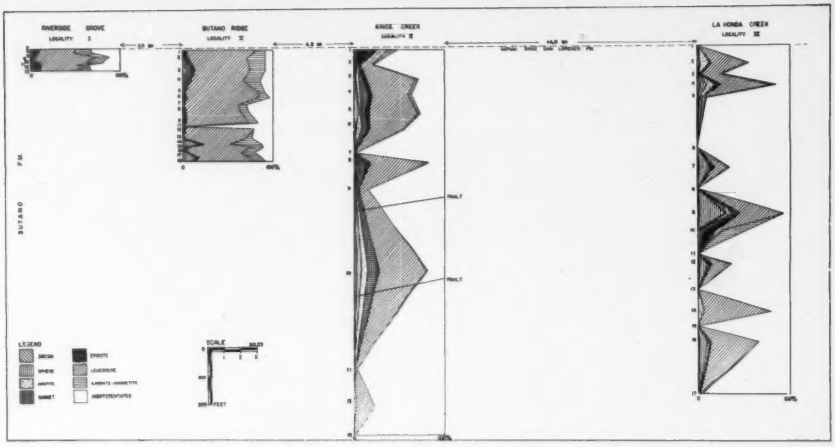

FIG. 8.—Stratigraphic variation of heavy mineral frequencies within the Butano Formation; screen size: −60+115 mesh.

the sharp increase in zircon frequency at Kings Creek and locally at La Honda Creek over that in the −250 mesh fraction of the same sections. Leucoxene and ilmenite decrease in frequency where zircon increases; therefore, it appears that zircon has been concentrated in the Kings Creek and La Honda Creek sections by removal from this size fraction of relatively unstable minerals such as sphene, ilmenite, and leucoxene. Ilmenite may have been removed by sorting and sphene and leucoxene by fracture and breakage into finer particle sizes. This is supported by an anomalous increase in leucoxene content in the −250 mesh fraction of the high-zircon samples at Kings Creek and La Honda Creek.

With the exception of this zircon anomaly, lateral variations in the −115+250 mesh size fraction are very similar to those in the −250 mesh fraction.

Figure 8 shows the same basic features as the other two figures except for increasing frequencies of pyrite and hematite, which account for all peaks of undifferentiated material. Leucoxene frequency is higher than in either of the two finer size fractions and is accompanied by lower ilmenite frequency; this is particularly noticeable at Riverside Grove and Butano Ridge. Zircon, apatite, sphene, and garnet frequencies are all lower than in the corresponding finer size fractions.

Figures 9 through 11 illustrate stratigraphic variations of mineral frequencies within the Vaqueros Formation. These sections are more complete than those of the Butano Formation and lack the distortion caused by pyrite and hematite which prevails in northern sections of the Butano Formation. For these reasons more accurate observations can be made regarding vertical and lateral mineral variations. In figure 9 vertical variation in mineral frequencies of zircon, apatite, garnet, leucoxene, and ilmenite is generally slight. Epidote, however, is much more abundant at East Big Basin and Saratoga Summit than in any other section of Vaqueros or Butano Formations, and its vertical variation is erratic. Sphene is much more plentiful and shows much less vertical variation in these Vaqueros sections than in the Butano Formation. Its most significant vertical variation occurs at Saratoga Summit where it disappears from the lower part of the section, although it has a high frequency in the upper part. Apatite frequency is not so high in the Vaqueros Formation as it is in the Butano Formation at Kings Creek and La Honda Creek; as in the Butano Formation, however, it increases with decrease in grain size.

In the upper part of the fine grained San Lorenzo Formation at Wildwood it comprises up to 25 percent of the heavy minerals.

Zircon, apatite, and garnet show very little lateral variation in frequency. Epidote is abundant at East Big Basin and Saratoga Summit but rare to absent at Wildwood and Peters Creek; this variation is probably a function of both progressive sorting and diagenetic solution. Sphene, leucoxene, and ilmenite show progressive lateral change between East Big Basin and Peters Creek. At East Big Basin sphene and ilmenite frequencies are high and leucoxene relatively low. Farther north at Saratoga Summit sphene remains abundant in the upper part of the section, although it is rare in the basal 150 ft; the leucoxene content increases and ilmenite decreases in comparison to the frequencies of these minerals at East Big Basin. The reduction in ilmenite content is probably caused in part by progressive sorting, but some of the decrease may be attributed to alternation to leucoxene. This accounts for the slight increase in leucoxene content over that at East Big Basin. The vertical variation of sphene and leucoxene in the Saratoga Summit section illustrates clearly the antipathetic relationship between these minerals.

At Peters Creek, still farther north, sphene content diminishes considerably, ilmenite all but disappears, and leucoxene frequency increases to such an extent, as a result of sphene and minor ilmenite alteration plus breakage from coarser grade sizes, that it becomes the predominant heavy mineral in the section.

Figure 10 illustrates mineral variations in the $-115+250$ mesh size fraction of the Vaqueros Formation. The major changes between this and the preceding -250 mesh fraction are lateral variations between East Big Basin and Peters Creek. The decrease in ilmenite frequency between East Big Basin and Saratoga Summit appears to be primarily a function of sorting and reduction to finer particle sizes rather than alteration because leucoxene content shows no increment where ilmenite decreases, as it does in the -250 mesh fraction.

The abrupt increase in zircon and garnet towards the base of the Saratoga Summit section and at Peters Creek, is probably a result of concentration of these two minerals

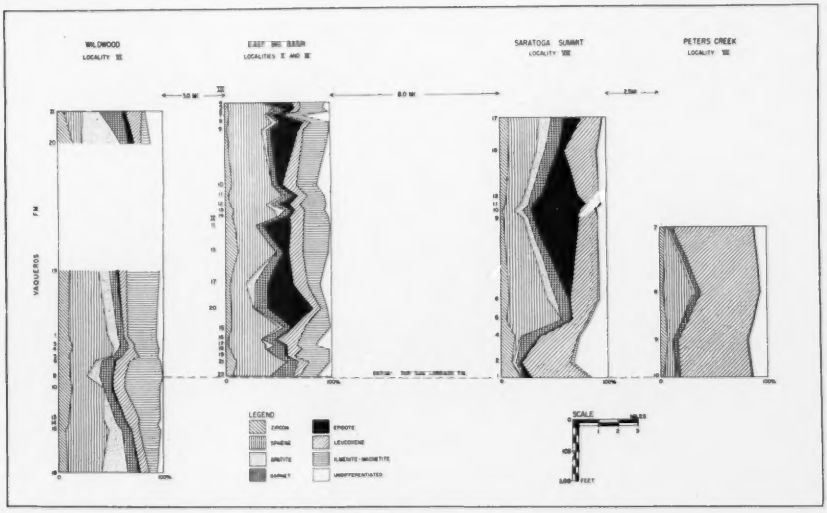

FIG. 9.—Stratigraphic variation of heavy mineral frequencies within the Vaqueros Formation; screen size: -250 mesh.

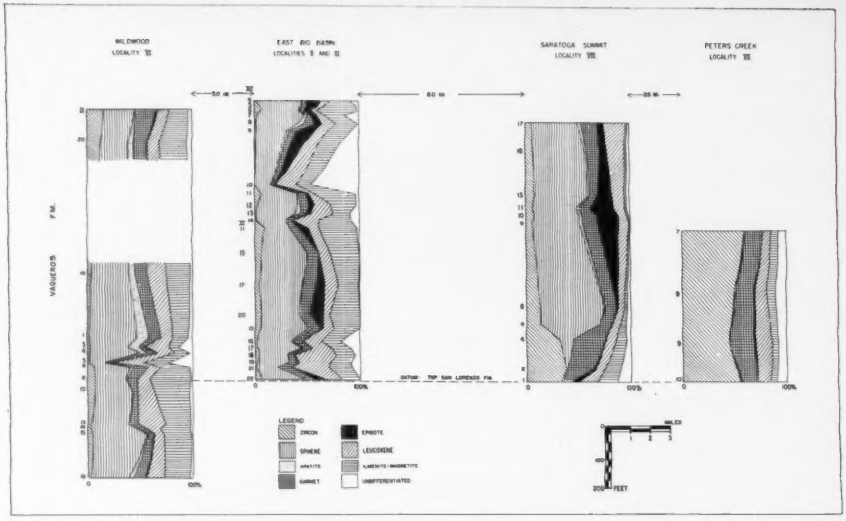

FIG. 10.—Stratigraphic variation of heavy mineral frequencies within the Vaqueros Formation; screen size: −115+250 mesh.

by removal of unstable sphene. Breakage of sphene into smaller particle size and alteration to leucoxene may have assisted this concentration. As in the case of anomalous increment in zircon content in the Butano Formation, the −250 mesh fraction shows a sharp increase in leucoxene towards the base of the Saratoga Summit section and at Peters Creek. Most of this is probably caused by normal lateral variations and alterations in the −250 mesh fraction, but some of the increase may well be caused by alteration and reduction in particle sizes of the coarser size fractions.

Ilmenite and magnetite frequencies are combined in these figures (see legend of figs. 6 through 11), but in most cases ilmenite is considerably more abundant than magnetite and is responsible for most of the variations in frequency of the ilmenite-magnetite combination. However, magnetite increases significantly in the coarser size fractions of sands in the lower part of the Saratoga Summit section and becomes a major heavy mineral in the −115+250 mesh fraction and the predominant heavy mineral in the −32+60 and −60+115 mesh fractions. This magnetite flood is discussed further under the heading "Provenance."

Figure 11 illustrates the mineral variations in the −60+115 mesh size fraction of the Vaqueros Formation. Zircon, apatite, and epidote decrease in all sections compared to the situation in the finer grade sizes; garnet and sphene show no distinct variation with increase in grain size; leucoxene increases and ilmenite decreases in comparison to their frequencies in the −115+250 mesh fraction.

The lateral variations are essentially the same as those noted in the −250 mesh fraction, namely progressive sorting and alteration of ilmenite and sphene towards the north with increasing distance from shore and source.

PROVENANCE

The heavy minerals of the Butano, San Lorenzo, and Vaqueros Formations in the Santa Cruz Mountains were derived from at least three and possibly four distributive provinces: (1) Ben Lomond quartz diorite and adjacent metamorphic rocks; (2) pre-Tertiary rocks located on the north side of the San Andreas fault; and (3) Montara quartz diorite and metamorphic rocks. A

sedimentary terrane which may have contributed some minerals to these formations occurs along the present coastline west of Butano Ridge (fig. 1) where Cretaceous rocks are now exposed. The areal distribution in the subsurface of these Cretaceous rocks is unknown at present; hence the extent of their contribution is highly conjectural.

The Montara province undoubtedly contributed much sediment to the northern part of the Tertiary basin, but its influence on sedimentation in the area of this study was probably minor. The major sources of the heavy minerals dealt with here, therefore, are: (1) the Ben Lomond province and (2) the pre-Tertiary province on the north side of the San Andreas fault.

Spotts (1958, personal communication) has recently completed a study of heavy minerals from a number of igneous masses in and adjacent to the Coast Ranges of central California including the Ben Lomond and Montara quartz diorites. The principal minerals which he found in these two masses are: zircon, hornblende, sphene, clinozoisite-epidote, apatite, biotite, ilmenite, and leucoxene with lesser amounts of garnet, allanite, and magnetite. This suite, with the exception of hornblende, is almost identical to the major types found in the lower Tertiary formations immediately adjacent to Ben Lomond. Spessartite-almandine garnet is present in some phases of the intrusive and is chemically very similar to the pink variety occuring in the sediments. Most of the colorless grossularite, together with much of the euhedral and dusty tourmaline in the sediments, were probably derived from metamorphic zones associated with this intrusive.

Minerals such as colorless zircon, hyacinth, rutile, and tourmaline, which display much evidence of abrasion, are indicative of more than one cycle of erosion and deposition. In the case of well-rounded hyacinth it is conceivable that three or four cycles occurred before final deposition in these sediments. Development of color is one of several modifications which zircon undergoes during the process of metamictization, and Tomita's (1954) work on colored zircons suggests that in order for the deep hyacinth color to be reached under maximum conditions of radiation bombardment, a period of more than 300 m.y. is required. The dark

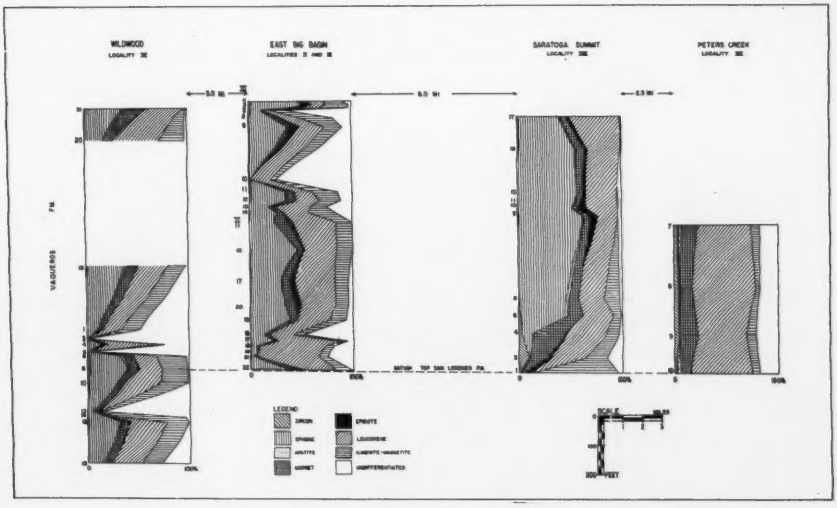

FIG. 11.—Stratigraphic variation of heavy mineral frequencies within the Vaqueros Formation; screen size: −60+115.

violet to almost opaque character of some of this hyacinth or malacon suggests an original Precambrian source with possibly many cycles of sedimentation before final deposition in the Tertiary sediments.

Amphiboles and pyroxenes are abundant minerals in the Ben Lomond and Montara quartz diorites (Spotts, 1958, personal communication), but both are exceedingly rare in these Tertiary sediments. A comparison between minerals from hard, calcareous sandstone concretions and those from laterally adjacent uncemented sands failed to reveal any increase in frequency of amphiboles or pyroxenes in the cemented sandstones. A similar study made by Bramlette (1941) revealed a marked increase in frequency of unstable minerals in most well-cemented rocks, which indicated to him removal of unstable constituents from adjacent permeable rocks by intrastratal solution. He concluded that diagenesis was halted locally at a very early stage by the formation of impermeable calcareous concretions through which solutions could not percolate. If Butano and Vaqueros concretions formed shortly after deposition of the sands, it must be assumed that unstable amphiboles and pyroxenes were never present to any extent in these sediments. Russell (1937) has shown that these minerals are sufficiently stable to withstand long distances of transport; therefore, the most logical conclusion regarding their absence from the sands is that they were destroyed by weathering at the source.

Glaucophane is a very rare constituent of both Butano and Vaqueros Formations, but its presence alone suggests that some of the minerals in these sands were derived from glaucophane schists and other rocks of the Franciscan Series (Taliaferro, 1943). The extent of the contribution made by this pre-Tertiary Franciscan terrane is doubtful; on the basis of glaucophane frequency alone, it would appear slight. On the other hand, the proximity of this terrane to the Tertiary sedimentary basin, in addition to the abundance of recycled minerals in the sediments, suggests that it may have contributed more sediments than the frequency of glaucophane would indicate. Conditions of weathering on the northeast side of the San Andreas fault were probably very similar to those prevailing at Ben Lomond, since distance between the two terranes was small. The same processes that destroyed the amphiboles and pyroxenes at Ben Lomond, therefore, may well have been responsible for the destruction of glaucophane and other unstable minerals of Franciscan rocks before they could be carried to the site of deposition.

Right lateral movement along the fault has been active intermittently throughout all of Cenozoic time, so that the present exposures of these pre-Tertiary strata are slightly south of those locations from which they contributed material to Tertiary sediments.

The flood of magnetite in the coarse fractions of sands in the lower part of the Saratoga Summit section is accompanied by an increase in the frequency of diopside in the same size fractions. This locality is closer than any other to the pre-Tertiary (Franciscan) terrane; hence it is reasonable to assume that the magnetite and diopside were derived from serpentine or other basic igneous rocks of the Franciscan Series. The relatively large grain size of these two minerals is probably a result of differential sorting.

Tourmaline, although variable in color, habit, and inclusions, may not be so accurate a source indicator here as it is in other areas (Krynine, 1940; Pettijohn, 1957, p. 513). Certainly well-rounded grains and those containing dusty, carbonaceous inclusions may accurately identify the type of rock from which these varieties were derived, but Staatz and others (1955) have shown that considerable chemical and color variation in tourmaline may occur between the wall and core of a single pegmatite.

The colors and shapes of tourmaline grains in Butano and Vaqueros sands, plus the character of included material, suggest three major parent rock types: (1) high rank metamorphic rocks, (2) older sedimentary formations, and (3) pegmatites or other acid igneous rocks. (1) and (3) are probably associated more commonly with the Ben Lomond quartz diorite, whereas (2) is more apt to occur in the pre-Tertiary sedimentary terrane, although some reworked tour-

maline grains may have been derived also from metamorphosed sediments around Ben Lomond.

AUTHIGENESIS

The following heavy minerals have formed at the site of deposition either during or after accumulation of the sediments: leucoxene-anatase, pyrite, hematite, barite, dolomite, and cerussite. Not all of these minerals are entirely authigenic, however; much of the leucoxene is undoubtedly detrital, particularly the well rounded, compact, porcellaneous grains (Tyler, 1936; Tyler and Marsden, 1938) which are widespread throughout these sediments.

Authigenic leucoxene-anatase varies from soft, earthy particles to aggregates of finely crystalline anatase which frequently forms secondary outgrowths from white, cryptocrystalline leucoxene nuclei (Gilligan, 1919; Wilgus, 1933). These grains are much too angular and fragile to have survived much abrasion during transport. The lateral stratigraphic relationship between sphene, ilmenite, and leucoxene, which has already been discussed, further suggests diagenetic alteration rather than alteration at the source.

Weathering of the sands may be responsible for some sphene alteration, but this is considered minor as most exposures have been subject to similar degrees of weathering; sphene-rich, leucoxene-poor sediments occur in the same stratigraphic interval as leucoxene-rich, sphene-poor sediments only a short distance apart. In addition, unweathered Butano Formation core samples contain much leucoxene as well as unaltered sphene.

Higgins and Carroll (1940) have suggested that authigenic anatase, brookite, and rutile are more apt to form in an acid or reducing environment some distance from land in still waters of the open ocean. This agrees with the conditions under which much of the leucoxene and anatase of these sediments may have formed. The sections of Vaqueros strata rich in leucoxene are those at Saratoga Summit and Peters Creek, both of which are more distant from the shore (and source) than those sections of the same formation containing little leucoxene. Open sea conditions appear to have prevailed because both pyrite and its alteration product, hematite, are rare in these Vaqueros Formation sand sections.

Another possibility, which deserves mention with respect to the alteration of sphene to leucoxene, is the effect of intrastratal solution on the sediments between early Miocene and Recent time. Many grains of garnet, apatite, sphene, and epidote are highly etched and corroded as a result of these post-depositional solutions (Smithson, 1941, 1942; Bramlette, 1929), and the formation of anatase or leucoxene may well have occurred after consolidation of the sediments.

The authigenic nature of pyrite and hematite has been discussed previously and needs no further comment here.

Barite and dolomite are very restricted in distribution, and their very angular and frequently irregular shapes suggest these minerals are authigenic.

Little is known of the occurrence of sedimentary cerussite. The angularity and apparent fragility of the mineral suggest that it, like barite and dolomite, is also authigenic. Galena, occurring in fresh, cleavage fragments, is a very rare constituent of these Tertiary sands; locally it may have been concentrated in sufficiently large amounts to form the more abundant cerussite by alteration. The presence of cerussite in unweathered core samples of Butano sand indicates that this mineral is not formed as a result of weathering.

CONCLUSIONS

The Ben Lomond distributive province was the major source of the heavy minerals which occur in these lower Tertiary sedimentary rocks. However, an indeterminate amount of reworked material in addition to more diagnostic species appear to have been derived from older sedimentary, metamorphic, and basic igneous rocks of the pre-Tertiary Franciscan terrane northeast of the San Andreas fault.

Stratigraphic variations of mineral frequencies in the Butano and Vaqueros Formations result from four major processes:

1.—Differential sorting, whereby heavy constituents, like ilmenite, settle out close to the shore and source while lighter minerals,

such as apatite, are carried farther out into the basin before being deposited.

2.—Relative concentration of stable minerals, like zircon, by removal of relatively unstable types, such as sphene; removal may be accomplished by breakage into finer particle sizes, by alteration, or solution.

3.—Diagenetic alteration of minerals such as ilmenite and sphene to leucoxene (or anatase); diagenesis may occur shortly after deposition, or after consolidation of the sediments.

4.—Changing conditions of erosion and weathering at the source plus changes in the mode of transport of minerals to the site of deposition. This process applies particularly to mineral variations in a vertical plane.

The use of heavy mineral assemblages alone as a means of correlating Butano and Vaqueros Formations throughout the Santa Cruz Tertiary basin is limited.

No distinctive mineral species are restricted to one formation, although relative abundances of some species differ between formations. Apatite, for example, is more abundant in finer grained rocks of the Butano and San Lorenzo Formations than in the Vaqueros Formation. Sphene, on the other hand, is much more abundant in Vaqueros sands than in those of the Butano Formation, particularly in the uppermost 300 ft of the Butano Formation. Epidote is locally more common in the Vaqueros Formation compared to the Butano Formation, but its stratigraphic distribution is erratic. Pyrite and hematite, like apatite, are more characteristic of finer grained Butano sediments.

Heavy minerals may serve to distinguish between these two formations in sections representing greater distance from shore, as in the Butano Formation at La Honda Creek and the Vaqueros Formation at Peters Creek. However, in order to distinguish accurately and completely between these formations throughout the entire basin, comparison of sediments on the basis of textural (grain size, sorting, roundness, etc.) and compositional ("heavy" and "light" minerals) analyses in relation to shorelines or source areas may be necessary.

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REFERENCES

Boswell, P. G. H., 1924, Petrography of the sands of the Upper Lias and Lower Inferior Oolite in the west of England: Geol. Mag. v. 61, p. 246–264.

Bramlette, M. N., 1929, Natural etching of detrital garnet: Am. Mineralogist, v. 14, p. 336–337.

———, 1941, The stability of minerals in sandstone: Jour. Sedimentary Petrology, v. 11, p. 32–36.

Branner, J. C., Newsom, J. F., and Arnold, Ralph, 1908, Santa Cruz Quadrangle, California: U. S. Geol. Survey, Folio 163.

Cogen, W. M., 1935, Some suggestions for heavy mineral investigations of sediments: Jour. Sedimentary Petrology, v. 5, p. 3–8.

Coil, F., 1933, Chemical composition of leucoxene in the Permian of Oklahoma: Am. Mineralogist, v. 18, p. 62–65.

Gilligan, A., 1919, The petrography of the Millstone Grit of Yorkshire: Geol. Soc. London Quart. Jour., v. 75, p. 251–294.

Higgins, H. G., and Carroll, Dorothy, 1940, Mineralogy of some Permian sediments from Western Australia: Geol. Mag., v. 77, p. 145–160.

Hutton, C. O., 1950, Studies of heavy detrital minerals: Geol. Soc. America Bull., v. 61, p. 635–716.

———, 1952, Accessory mineral studies of some California beach sands: U. S. Atomic Energy Comm., RMO 981, p. 1–112.

Krynine, P. D., 1940, Petrology and genesis of the Third Bradford Sand: Pennsylvania State Coll. Bull. 29, Mineral Industries, p. 1–134.

Pettijohn, F. J., 1957, Sedimentary rocks. 2nd Ed., Harper and Brothers, New York, 718 p.

Poldervaart, A., 1955, Zircons in rocks, Part 1: Sedimentary rocks: Am. Jour. Sci., v. 253, p. 433–461.

Prider, R. T., 1939, Some minerals from the leucite-rich rocks of the West Kimberley area, Western Australia: Min. Mag., v. 25, p. 383–387.

Russell, R. D., 1937, Mineral composition of Mississippi River sands: Geol. Soc. America Bull., v. 48, p. 1307–1348.

SMITHSON, FRANK, 1941, The alteration of detrital minerals in the Mesozoic rocks of Yorkshire: Geol. Mag., v. 78, p. 97–112.

———, 1942, The Middle Jurassic rocks of Yorkshire: A petrological and palaeogeographical study: Geol. Soc. London Quart. Jour., v. 98, p. 27–59.

STAATZ, M. H., MURATA, K. J., AND GLASS, J. J., 1955, Variation of composition and physical properties of tourmaline with its position in the pegmatite: Am. Mineralogist, v. 40, p. 789–804.

TALIAFERRO, N. L., 1943, Franciscan-Knoxville problem: Am. Assoc. Petroleum Geologists, v. 27, p. 109–219; esp. 159–182.

TOMITA, TORU, 1954, Geologic significance of the color of granite zircon, and the discovery of the Pre-Cambrian in Japan: Mem. Fac. Sci., Kyushu University, Ser. D, Geol., v. 4, p. 135–161.

TYLER, S. A., 1936, Heavy minerals of the St. Peter Sandstone in Wisconsin: Jour. Sedimentary Petrology, v. 6, p. 55–84.

TYLER, S. A., AND MARSDEN, R. W., 1938, The nature of leucoxene: Jour. Sedimentary Petrology, v. 8, p. 55–58.

WILGUS, W. L., 1933, Heavy minerals of the Dresbach Sandstone of western Wisconsin: Jour. Sedimentary Petrology, v. 3, p. 83–91.

WILLIAMS, H., TURNER, F. J., AND GILBERT, C. M., 1955, Petrography. W. H. Freeman and Company, San Francisco, 406 p.

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FIGS. 1–10, DECEMBER, 1960

PETROLOGY OF PARRY GROUP, UPPER DEVONIAN-LOWER CARBONIFEROUS, TAMWORTH-NUNDLE DISTRICT, NEW SOUTH WALES[1]

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ABSTRACT

The Parry Group conformably overlies the Tamworth Group in the Tamworth Trough sequence of northeastern New South Wales. It consists dominantly of olive-green chloritic mudstones together with lithic labile graywacke and sandstone, feldspathic graywacke, argillaceous and lithographic limestone, and polymictic conglomerate. The detritus is thought to have been derived from an andesitic island arc which contained local exposures of older sediments, granite, and acid volcanics. The lithic labile arenites consist dominantly of volcanic rock fragments and plagioclase, generally albitised but occasionally unaltered andesine, with some clinopyroxene, amphibole, chlorite, opaques, and minor quartz. The modal composition of these rocks shows a restricted range of variation through the sequence, which suggests that changes of composition of source areas were not marked during the period of deposition of the sequence.

INTRODUCTION

The Parry Group (formerly the Lower Burindi and Barraba Series) occupies the Upper Devonian and Tournaisian portions of the sequence in the Tamworth Trough of northeastern New South Wales (Crook, 1960b). The group, which is subdivided into three formations and several members (table 1), attains a maximum thickness of approximately 18,700 feet. It conformably overlies the Tamworth Group, the petrology of which has been described by Crook (1960c).

The group consists mainly of olive-green chloritic mudstone together with feldspathic and lithic labile arenite, argillaceous and lithographic limestone, and polymictic conglomerate. All these rock types are represented in the Goonoo Goonoo Mudstone, certain of its members consisting of lithographic limestone or tongue-like masses of lithic labile arenite or polymictic conglomerate (Crook, 1959). Some of these members contain a feldspathic labile arenite component. In the upper parts the arenites are sandstones, in the lower parts they are graywackes in the terminology of Packham (1954) as expanded by Crook (1960a). This terminology is used throughout this paper. The Wombramurra Formation is dominantly polymictic conglomerate and lithic labile graywacke with minor feldspathic labile graywacke and mudstone. The Baldwin Formation consists dominantly of lithic labile graywacke and mudstone with some siltstone, occasional lenses of argillaceous limestone, and rare polymictic conglomerate.

The terminology and techniques used in this study have been described (Crook, 1960c). Refractive indices of various minerals are included in table 3.

MODAL ANALYSES

Modal analyses of a small selection of sediments (including three from the Tamworth Group) have been prepared (table 2) using a "Swift" point-counter. Chayes' method (1956) was followed, some 1800 points arranged in a symmetrical grid being counted. The translation distances between points and rows of points were fixed at 0.167 mm and 1 mm, respectively.

The restricted variation in composition and clear separation of the feldspathic and lithic labile arenites (figs. 1 and 2), is bourne out by examination of about one hundred unanalysed slides. This suggests that changes in composition of source areas were

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TABLE 1.—*Stratigraphic subdivision of the Parry Group*

		Western Region		Eastern and Southern Regions	
Lower Carboniferous	Visean	"Lower Kuttung Group" (CK)		(not preserved)	
Lower Carboniferous	Tournaisian	PARRY GROUP	Goonoo Goonoo Mudstone (Clg)	Goonoo Goonoo Mudstone (Clg)	Pyramid Hill Arenite Members (Clp)
		-Boiling Down Sandstone Member (Clbs)			-1 -2 -3 -4 -4a -5 -6 -7
		-Gowrie Sandstone Member (Clgs)			-8 -9 -10
		-Turi Graywacke Member (Clt)		-Benama Graywacke Member (Clbg)	P- Q- R- S- T- U- V- Va- W- X- Y- Z-
		-Garoo Conglomerate Member (Clgc)		-Wombramurra Formation (Clw)	
		-Scrub Mountain Conglomerate Member (Cls)		-Scrub Mountain Conglomerate Member (Cls)	
		-Kiah Limestone Member (Dlk)		-Hyde Graywacke Member (Clh)	
Upper Devonian		Baldwin Formation (Dub)		Baldwin Formation (Dub)	
Middle Devonian		not exposed		Tamworth Group	

TABLE 2.—*Micrometric analyses, in percentages*

Number	Unit	Quartz	Feldspar	Rock fragments	chlorite	Matrix	Carbonate	Heavies	Ferro-magnesians	Cement	No. of points Counted
R799	Clg	8.8	67.5	2.5	1.7		1.4	0.4		17.8	1807
R806	Clg	6.9	48.6	5.4	4.9	13.7	10.1	3.1		7.2	1714
R808	Clg	4.1	67.0	3.1	(+heavies)		6.1			19.7	1823
R809	Clp_1	1.0	24.4	50.5	1.3	10.9		1.9	1.6	8.4	1824
R818a	Clbs	1.2	22.5	58.3	1.9	8.6		0.5		7.0	1810
R824	Clp_6	0.5	20.6	55.1	4.9	16.7		0.5		1.4	1820
R833	Clgs	0.4	23.7	51.3	1.0	10.9	2.2	0.2	0.6	9.7	1807
R835	Clp_U	1.2	26.9	56.9	0.9			0.6		13.6	1803
R856	Clp_9	1.6	28.6	48.9	1.7	5.4	2.7	1.3		9.8	1803
R860	Clp_Z	1.5	17.8	77.8	1.0			1.0	1.0		1776
R863	Clt	0.2	35.1	47.0	3.7	9.5	0.3	4.1			1811
R867	Clgc	1.5	16.5	67.1	0.9	7.6		0.9	0.4	4.9	1810
R871	Clw	1.2	19.4	65.1	0.4	6.6		0.3	1.7	5.3	1806
R874	Clw	4.6	55.7	17.4	0.6	13.5	3.6	0.8		3.9	1806
R880	Cls	0.3	17.3	66.8	1.5	7.8		1.0	0.8	4.5	1801
R898	Dub	0.6	15.9	66.4	2.8	7.2	0.3	0.6		6.4	1803
R903	Dmy[3]	0.3	30.8	51.4	1.0	6.8		0.3		9.4	1801
R926	Dmlg[3]	0.9	16.4	61.5		5.7		0.4	1.0	14.1	1800
R928	Dms[3]	0.1	16.4	70.3		3.2		1.4	0.7	8.0	1803

[3] For description see Crook (1960c).

not marked during the period represented by the sequence, and thus minimises the dangers in generalising from so few data.

PETROGRAPHY

Feldspathic Labile Arenites

These fall into three main groups. The first (R792, R800, R806, R808, R866, R868 and R878) is typically richly feldspathic with some quartz, minor chlorite, calcite and detrital accessories, and a prominent early diagenetic calcite cement (fig. 3) and consists of calcareous feldspathic graywackes, often with excellent graded bedding. In general, they are well sorted and medium to coarse grained, the finer examples (R868, R878) containing more chloritic material. The number of grain contracts per grain is rather low, loose-packing being particularly noticeable in the finer types. Angular grains are common, but many rather better rounded grains occur. Sphericity averages 0.6.

Quartz grains in general are simple and unstrained, although a few strained grains, some composite, have been noted. Embayments occur and may be filled with calcite, which also fills fractures and may partially replace the grains. Fluid inclusions, often in trails, and high relief, acicular and chlorite inclusions occur.

TABLE 3.—*Refractive Index (n_Y) determinations*

Stratigraphic Unit	U.N.E. Coll. No. R.	Detritals		Diagenetic		
		Pyroxene	Feldspar	Albitised Feldspar	Feldspar replacing Ca. Feldspar	Zeolite replacing Ca. Feldspar
Clp_1	809	1.696	1.560	1.534	1.534	
Clp_2	810	1.696		1.532		1.515
Clp_3	811	1.697	1.551	1.534		1.505
Clp_{3a}	816		1.552			1.514
Clp_4	817			1.533		
Clp_{4a}	819		1.551			
	821					1.514
Clbs	818a			1.534		
Clp_5	822		1.558			1.521
Clg below Clp_5	794		1.550			
Clp_7	827			1.534		
Clgs	832	1.691		1.532		
Clg above Clp_8	796		1.550			1.510
Clp_8	841			1.534		
?Clp_8	846	1.697				
?Clp_9	854			1.534		
Clp_{10}	859	1.696				
Clg above Clbg	801		1.555			
Clt	864					1.514
	863			1.535		
Clbg	865			1.533		
	866		1.549			
Clgc	868		1.545	1.534		
Clp_R	828	?1.644?		1.533		
Clpv	837			1.534		
	836	1.692				
	838		1.549		1.534	
Clpw	849		1.549	1.534		
Clpz	860	1.696		1.534		
Clw	873		1.549	1.533		1.520
	871	1.692				
Clg below Clw	802			1.534		
Cls	878		1.546	1.534		
Dub	894			1.532		
	897		1.552	1.533	1.532	
	899	1.694				
	888			1.534		

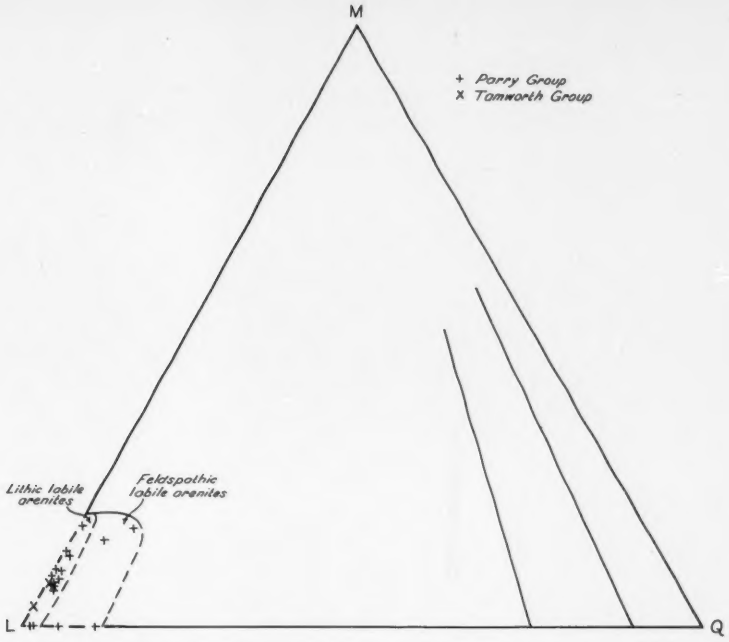


FIG. 1.—MLQ diagram of arenites calculated on cement-free, carbonate-free basis.

Feldspar is generally a clear, moderately calcic plagioclase, two determinations (R866, R868) giving An_{26} and An_{34}. It usually shows multiple twinning, is often zoned, and is always veined either by albite or occasionally a zeolite. In a few cases this alteration is almost complete, the resulting plagioclase being albite (An_3). Such grains show sericitisation and slight clouding. Commonly many grains are fractured, the fractures containing calcite or chlorite. Chorite and apatite inclusions occur, and there may be partial replacement of the grains by calcite.

Chlorite is usually present as irregular yellow-green structureless patches, containing apatite, opaque, or calcite inclusions. In the more chlorite-rich types, the chlorite occurs as well-rounded regular grains.

Detrital *calcite*, some clearly of organic origin, is common. Crinoid, brachiopod, and bryozoan fragments have been observed. Replacement by glauconite? has been noted (R868).

Accessories comprise biotite (at times altering to chlorite), apatite, iron-opaques, epidote, pyroxene, yellow-brown amphibole, and possible sphene.

Rock fragments are a very minor component. A small amount of textural andesite and textural basalt, a red-brown glassy volcanic with feldspar laths, some other fine volcanics, and a small amount of siltstone occur.

Diagenesis: In all cases calcite is the dominant cement. It varies from coarsely to very finely crystalline, occasionally appearing like a matrix. In some slides the calcite may be brown; in others a small amount of chlorite, similar to that occurring as fragments, occurs as a cement.

The second group of feldspathic labile arenites (R794, R801, R864) are best termed calcareous tuffaceous feldspathic labile gray-

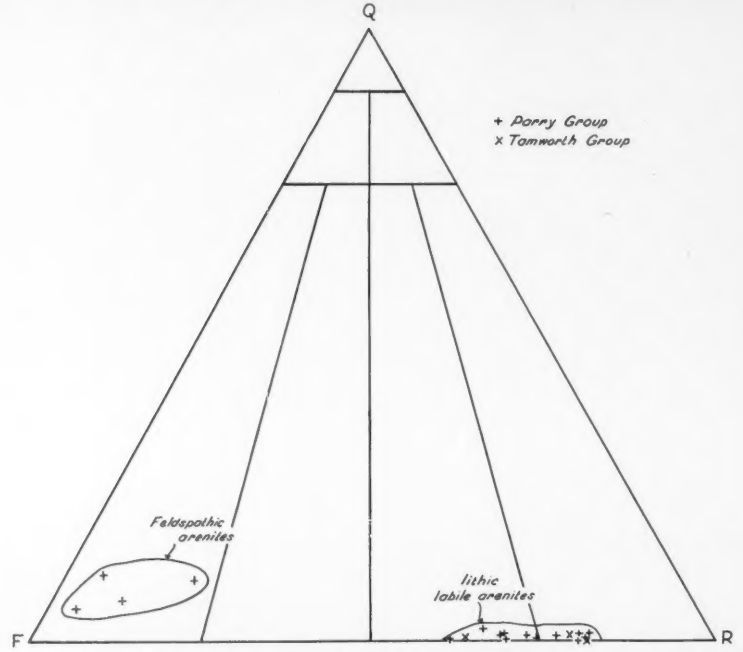


FIG. 2.—QRF diagram of arenites calculated on cement-free, carbonate-free, matrix-free basis.

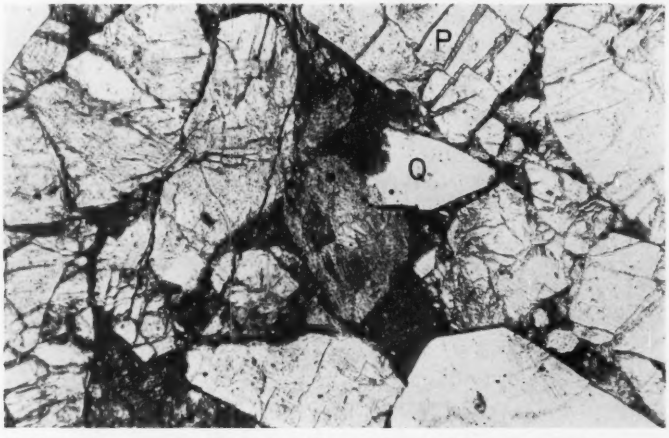


FIG. 3.—Feldspathic graywacke (R806) from Goonoo Goonoo Mudstone, showing quartz (Q) and oligoclase-andesine (P) with a calcite cement. Calcite fills fractures in the plagioclase grains (×38).

wackes because they contain pumiceous material or shards replaced by calcite. Although R801 is strictly not a feldspathic labile graywacke (because of its high percentage of replaced pumice fragments), its close similarities to these rocks warrant considering it at this point. R864 contains abundant angular amphibole but no definite shards. However, its abundant calcareous matrix-cum-cement, in which the detrital grains float, shows structures suggestive of replaced glass.

These rocks are generally coarse and moderately sorted. Constituents are usually angular and of variable sphericity. Calcite cement is abundant, and R794 also contains an aggregate polarising matrix, probably of glass.

Quartz is absent. The *feldspar* is andesine (An_{36}–An_{46}), similar to that in the first group. It is veined by laumontite ($2V(-)$sm.,$r < v$ appreciable, $n_Y = 1.514$) and probably albite and at times is extensively replaced by calcite. Apatite, chlorite, and amphibole inclusions occur.

Amphibole is abundant in R864. It is pleochroic from greenish-yellow to brownish green, contains opaque inclusions, and is extensively replaced along cleavages by chlorite and calcite.

Rock fragments: Minor siltstone, some fluidal vitric volcanics, and felty volcanics are present. In R801 replaced pumice is abundant. It consists of aggregates of calcite, showing variations in grain size, vesicular structure, traces of shard-like bodies and occasional feldspar laths.

Accessories: Minor detrital calcite similar to that previously described, apatite, and iron-opaques have been noted.

Shards largely replaced by calcite ($n_O = 1.658$) occur in R794 (fig. 4).

Diagenesis: The cement is calcite, that in R801 being initially colourless but becoming pale brown.

The third group is comprised of non-calcareous feldspathic graywackes (R793, R799, R803, R874) similar to the first group but containing much less calcite and more rock fragments. Coarse and moderately to well sorted, they are more densely compacted than those previously described. Fragments tend to be subrounded and have a sphericity of approximately 0.7. Matrix is generally prominent.

The quartz and feldspar is similar to that previously described, although albitic plagioclase is more common. It may contain muscovite in fractures and at time poikilitically encloses chlorite blebs.

A similar assemblage of accessories together with calcite occurs. Chlorite again

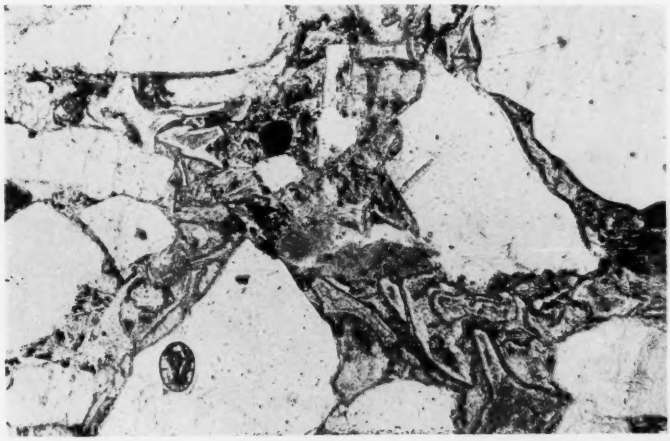


FIG. 4.—Tuffaceous feldspathic graywacke (R794) from Goonoo Goonoo Mudstone, below Member 5 of Pyramid Hill Arenite. Shards are replaced by calcite which also acts as cement (×50).

occurs as structureless irregular patches with albite and calcite associated.

The suite of rock fragments is more varied, volcanic fragments (with albite) being dominant. Types encountered are: felty, pilotaxitic, trachytic, vesicular vitric, ophitic, textural andesite, and textural basalt. Dolerite fragments with dendritic feldspars occur in R803. Radiolarian siltstone also occurs.

Diagenesis: Species observed acting as cement are chlorite, quartz, calcite, albite, muscovite, and ?pumpellyite. No veins have been seen.

Argillaceous Limestones

These occur as fine dark lenticular masses in the mudstones and are similar to those in the Yarrimie Formation (Crook, 1960b) but apparently lack radiolaria. Constituents are silt-sized quartz, plagioclase, chlorite, opaques, epidote, and brown tourmaline scattered through a finely crystalline mass of calcite of early diagenetic origin.

Lithic Labile Arenites

These are of remarkably restricted composition as can be seen from figures 1 and 2. They are lithic or feldspatholithic arenites (figs. 5 and 6), both graywackes and sandstones being present, the latter in the upper parts of the sequence. Table 4 indicates the slides of this type examined and their stratigraphic position. These arenites are frequently medium to fine grained, although coarse grained examples are common. Sorting is rather variable, but two distinct groups occur, one moderately to well sorted, the other poorly sorted. The last group is more characteristic of, but is not confined to, the lower parts of the unit. Fragments usually show a sphericity between 0.5 and 0.8 and are dominantly subangular to subrounded, although grains showing a greater or less degree of rounding are not uncommon.

These arenites are comprised dominantly of rock fragments and plagioclase with appreciable quantities of chlorite, carbonate, amphibole, pyroxene, and also some quartz and iron-opaques. Accessory sphene-chlorite, epidote, and apatite are frequent. Matrix is usually absent; when present it is chloritic and not prominent. A cement, often chlorite or calcite, is usually present and may be abundant. The rocks generally show strong compaction, the grains being in close contact. This predates the development of the cement.

Quartz usually occurs as simple unstrained grains, although a few simple and rare composite strained grains occur. Embayed grains are uncommon (R871, fig. 7) as are broken rounded grains. Fluid inclusions,

FIG. 5.—Lithic graywacke (R867) from Garoo Conglomerate Member. Note abundance of rock fragments (×46).

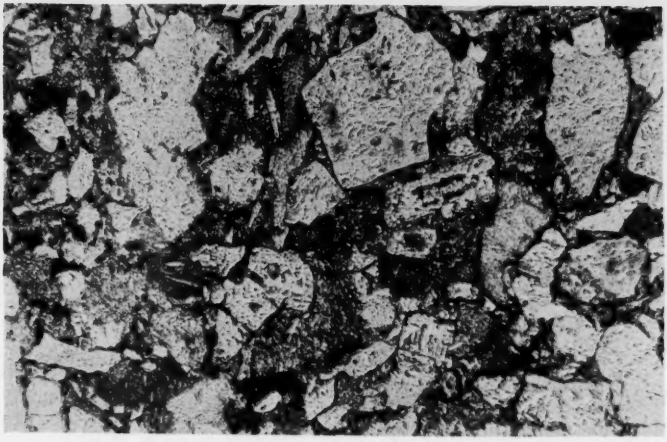


FIG. 6.—Feldspatholithic graywacke (R856) from Pyramid Hill Arenite, Member 9. Note abundance of feldspar in comparison with figure 5 (×46).

often in trails, are very common, and high relief inclusions are often encountered. Acicular and rod-shaped inclusions, dusty streaks, and inclusions of apatite, zircon, chlorite, muscovite, opaques, and tourmaline occur. Obscure striae have been noted on a few grains. In several cases orthoclase is associated with the grains. Replacement by calcite (R783) and marginal reaction with matrix occur.

Feldspar: Minor amounts of orthoclase, usually fairly heavily kaolinised, occur in many slides. Plagioclase is the dominant feldspar, being typically albite (An_2–An_4). It shows sparse multiple twinning, is usually very slightly clouded and flecked with sericite, and may contain inclusions of chlorite, calcite, or apatite. Less frequently more calcic plagioclase (An_{26}–An_{55}) occurs. It is generally clear, shows sharp multiple twinning and occasionally zoning, and is usually veined, at times extensively, by a zeolite (probably laumontite) in the higher parts of the sequence or by albite (An_2–An_4) lower in the sequence. Rarely chlorite inclusions occur, and occasional replacement by calcite has been noted. The albitic plagioclase may be extensively replaced by calcite, sericite, pumpellyite, prehnite, epidote, or rarely zeolite or muscovite.

Occasional grains of clear, untwinned feldspar of moderate relief, 2V(+)lg, have been noted in some slides. This variety, which simulates quartz, is identical with that described from the Yarrimie Formation (Crook, 1960b).

TABLE 4.—*List of lithic labile arenites from Parry Group and constituent formations and members*

Unit	Slide Numbers	Unit	Slide Numbers
Clp_1	R809	Clpz	R860, 861
Clp_2	R810	Clbs	R818a
Clp_3	R811	Clgs	R832, 833
Clp_{3a}	R812–816	Clt	R862, 863
Clp_4	R817, 818	Clgc	R867
Clp_{4a}	R819–821	Cls	R879–881
Clp_5	R822, 823		
Clp_6	R824	Clbg	R865
Clp_7	R827	Clg (above Clp_8)	R796
Clp_8	R841, 842	Clg (below Clp_8)	R797
?Clp_8	R843–847	Clg (below Clpz)	R798
?Clp_9	R853, 854	Clg (below Clw)	R802
Clp_9	R855, 856		
Clp_{10}	R858, 859		
Clp_R	R828	Clw	R870–873, 875–877
Clp_S	R829	Dub	R884–898, 900, 963
Clp_T	R830, 831		
Clp_U	R834, 835		
Clp_V	R836–838		
Clp_{Va}	R839, 840		
Clp_W	R848, 849		
Clp_X	R850–852		
Clp_Y	R857		

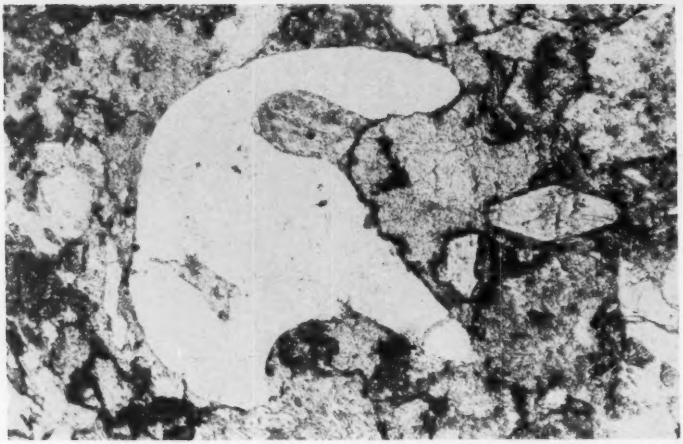


FIG. 7.—Deeply embayed grain of volcanic quartz in lithic graywacke (R871) from Wombramurra Formation. Grain of amphibole on right (×90).

Pyroxene often occurs and is usually tinted green, although a few brown-tinted grains have been noted. Refractive index determinations (table 3) and 2V(+)lg suggest it is a rather diopsidic augite. It is frequently replaced by decussate chlorite or calcite.

Amphibole also is widespread and is usually pleochroic from a pale greenish or yellowish brown to deep green or brownish green. Replacement by chlorite or calcite is not uncommon.

Calcite occurs as both inorganic and organic detritus (crinoid and brachiopod fragments). Calcite is abundant in only a few slides and even then rarely reaches 10 percent of the total.

Chlorite: A wide variety of optically negative chlorite occurs both as irregular structureless patches with feldspar, epidote, and apatite inclusions, and as regular grains, at times decussate (fig. 8). Colors are predominantly yellow green, pale green, and blue green.

Accessories: Grains of sphene-chlorite showing octahedral lamellae of sphene with interstitial chlorite (fig. 9) occur in several slides. These grains also occur in the Tamworth Group (Crook, 1960c). High in the sequence (Pyramid Hill Arenite Members 2 and 3) sphene-opaque grains occur, with opaque oxide occupying the interstices between the octahedral sphene lamellae instead of chlorite. Detrital apatite, green epidote, opaques, zircon, sphene, biotite, muscovite, prehnite, and ?pumpellyite have been encountered, the first three being common.

Rock fragments: A very wide range of fragments, largely volcanic, occur in these arenites. They usually contain albitic feldspar and much chlorite, frequently pseudomorphous after ferromagnesians. Some, however (R811, R813, R816, R845, R897), contain a more calcic plagioclase with hornblende and pyroxene similar to that encountered as free grains. Ferromagnesians occasionally occur in the albitic volcanics, amphibole being noted in textural andesite, and hyalopilitic, trachytic, pseudoclathrate, and pilotaxitic volcanics; pyroxene is found in hyalopilitic volcanics, textural andesite, and textural basalt. Skeletal sphene-chlorite grains, identical to the free grains, occur rarely in cryptofelsitic and vitric volcanic fragments (R837, R859). The textural varieties of rock fragments encountered are recorded in table 5. Minor dolerite and other volcanic fragments, which cannot be named satisfactorily, also occur.

An acid component is present, consisting of holocrystalline, spherulitic, and fluidal

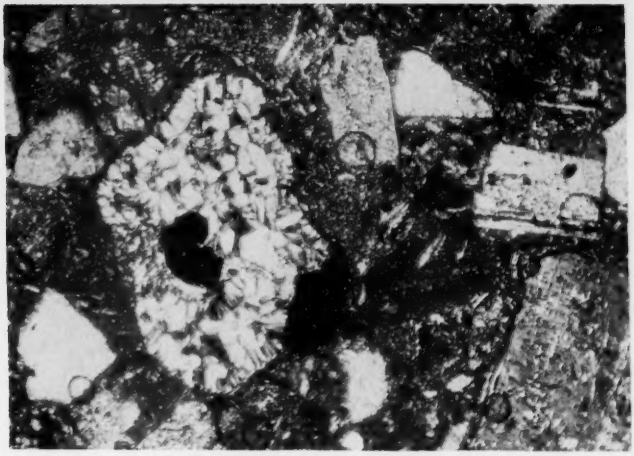


FIG. 8.—Decussate chlorite grain, with opaque inclusion, in lithic labile sandstone (R818) from Pyramid Hill Arenite, Member 4 (×100), crossed nicols).

rhyolites which are at times porphyritic. The holocrystalline types grade, with increasing grain size, into microgranites. Minor amounts of granite, at times micrographic (fig. 10), occur quite frequently.

A minor sedimentary component occurs in some slides. It consists of labile and quartz-rich arenites of types common in the graywacke suite and their siltstone equivalents. Siltstone with radiolaria (at times replaced by prehnite) has been noted (for example, R852), as have siltstone fragments of intraformational origin. Limestone occurs occasionally, and also quartzite, polymictic conglomerate, biotite hornfels, and vitric tuff.

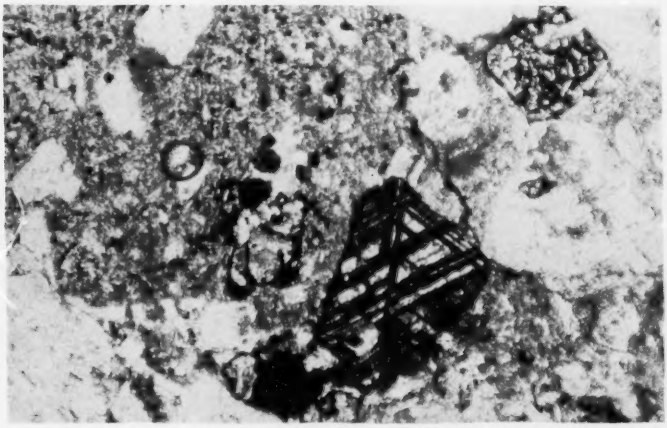


FIG. 9.—Skeletal grain consisting of sphene lamellae with interstitial chlorite in lithic labile graywacke (R850) from Pyramid Hill Arenite, Member X (×50).

TABLE 5.—*Varieties of rock fragments in detritus*

Unit	Goonoo Goonoo Mudstone	Wombramurra Formation	Baldwin Formation
Textural Variety			
textural andesite	x	x	x
textural basalt	x	x	x
hyalopilitic	p	x	p
hyalo-ophitic	x		x
intergranular	p	p	p
intersertal	x		x
pilotaxitic	p, v	p	p
trachytic	p	p	
subtrachytic	x	x	x
arabesquitic	p		p
pseudo-clathrate	p	x	p
perlitic	x		
fluidal	x		x
vitric	r, o, b	x	x
felty	p	x	p
opaque-rich	x		
orthophyric	x	x	x
ophitic	x		x
subophitic	x		x
cryptofelsitic	x		
spherulitic	x	x	
pumiceous		x	x

p—porphyritic; v—vesicular; r—red; o—orange; b—brown: x—present.

Diagenesis: Several minerals, either singly or in groups, may act as cement. Species observed are quartz, albite, chlorite, calcite, zeolite, prehnite, epidote, pumpellyite, and sphene. The latter occurs as granules scattered around the margins of the grains. Quartz and albite occur only in the Badwin Formation.

Occasional veins of quartz-carbonate, calcite, quartz-chlorite (R875), and prehnite-calcite (R893) have been noted.

Polymictic Conglomerates

These have been examined mainly in hand specimen. Volcanic pebbles are dominant (R899), and granite occurs in several units. Their constituent pebbles are probably of types similar to those in the lithic labile arenites.

Mudstones

These are usually silty. An X-ray powder photo of one specimen showed the presence of quartz, albite, and chlorite. They are probably dominantly chloritic.

Lithographic Limestone

Very fine gray limestone with scattered radiolaria and euhedral pseudomorphs (car-

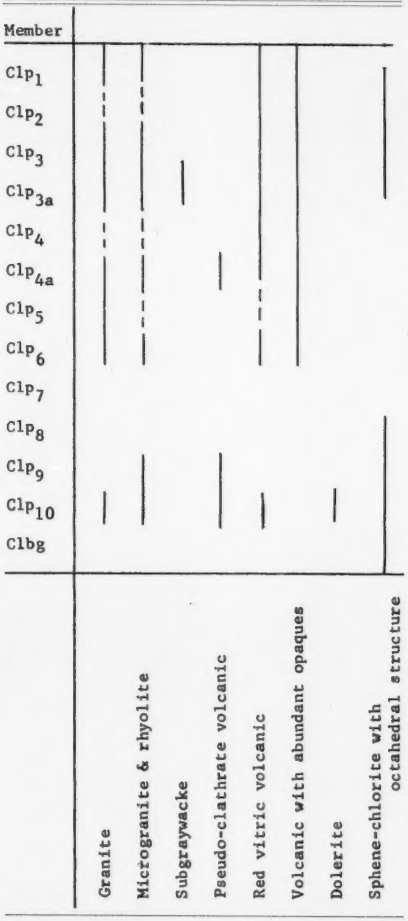
FIG. 10.—Fragment of micrographic granite in lithic labile graywacke from Baldwin Formation (×11, crossed nicols).

bonate plus micaceous material after probable albite) occurs in the Kiah Limestone Member. The pseudomorphs are prismatic, measure up to 0.5×2.5 mm, and stand out on weathered surfaces. Occasional detrital quartz grains and traces of stylolites have been noted.

TABLE 6.—*Petrography of Members of Goonoo Goonoo Mudstone.*

(A). *Southwest area*

Lithologic Features



CHARACTERISTICS OF INDIVIDUAL UNITS

Some of the characteristic features of several of the units are summarised in tables 6 to 9. Solid lines in these tables indicate that a large majority of slides examined carried the constituent; alternate dots and dashes indicate that a constituent occurs intermittently; and a broken line indicates that a constituent has not been observed but would be expected on the basis of its general stratigraphic distribution. The following points may be noted:

Pyramid Hill Arenite, Members 1–10 (Clp_1–Clp_{10}): Members 1 through 7 are lithic labile sandstones, 8 through 10 are lithic labile graywackes. Members 1 through 5 are generally much better sorted than Members 6 through 10. Members 2, 4, and 5 lack amphibole.

Pyramid Hill Arenite, Members P–Z (Clp_p–Clp_z): All are graywackes and are

TABLE 7.—*Petrography of Members of Goonoo Goonoo Mudstone*

(B) *Southern Area*

Lithologic Features

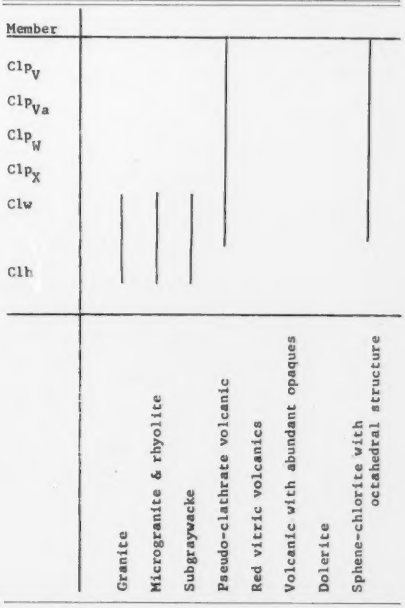
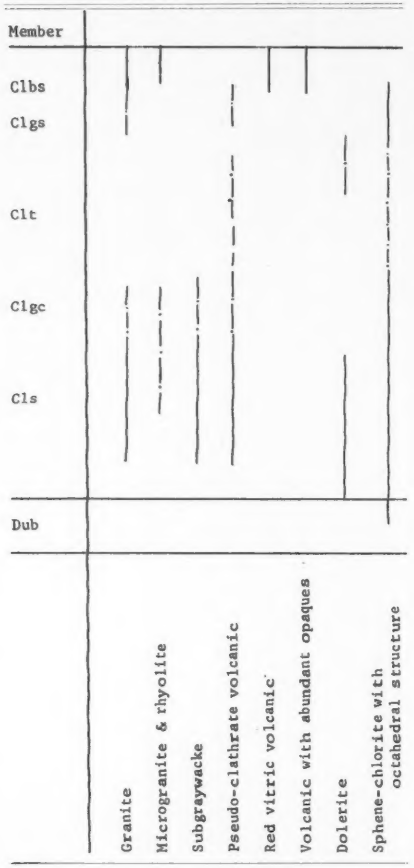


TABLE 8.—*Petrography of Members of Goonoo Goonoo Mudstone*

(C) *Western Area*

Lithologic Features



generally poorly sorted. Members W, X, and Y lack pyroxene and amphibole.

Boiling Down Sandstone Member (Clbs): Lithic labile sandstones lacking pyroxene and containing granite, rhyolite, a red vitric volcanic, and volcanics rich in opaques.

Gowrie Sandstone Member (Clgs): Well-sorted lithic labile sandstones containing minor granite, pseudoclathrate volcanics, and sphene-chlorite.

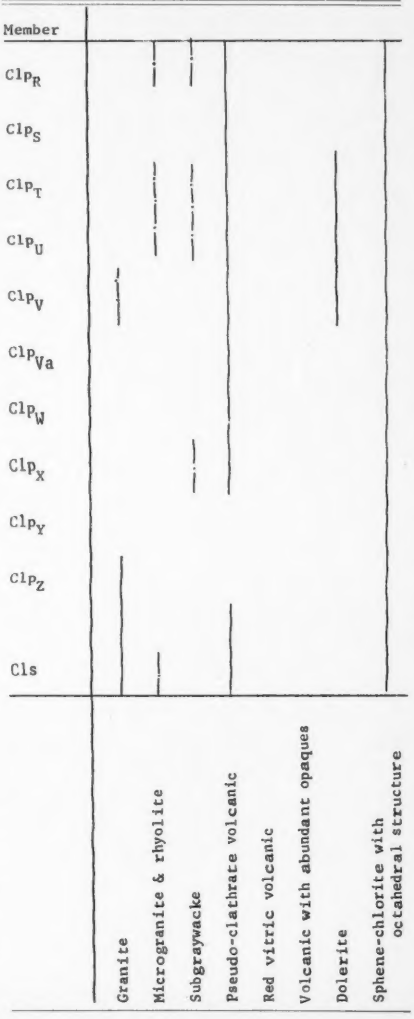
Turi Graywacke Member (Clt): Lithic labile graywackes lacking pyroxene and usually poorly sorted. Minor feldspathic labile graywacke occurs.

Garoo Conglomerate Member (Clgc): Con-

TABLE 9.—*Petrography of Members of Goonoo Goonoo Mudstone*

(D) *East-Central Area*

Lithologic Features



stituent graywackes are usually well sorted. Some feldspathic labile graywacke occurs.

Scrub Mountain Conglomerate Member (Cls): Sorting of constituent graywackes is good, and feldspathic labile graywacke occurs.

Benama Graywacke Member (Clbg): This lacks quartz but is otherwise without distinguishing features.

Hyde Graywacke Member (Clh): This lacks amphibole and pyroxene.

Wombramurra Formation (Clw): Calcic plagioclase is very rare, being encountered only in R873 (An_{34}), and is absent from the rock fragments. Detrital pyroxene and unaltered amphibole are usually present, and sphene-chlorite is common. There is a minor acid volcanic component, including spherulitic rhyolite. Sedimentary detritus is rather more common than elsewhere in the Parry Group.

Baldwin Formation (Dub): This consists of lithic labile graywackes, most of which are poorly sorted. However, those from the Timbumburi district (R885, R888, R891, R892) are well sorted. Relics of andesine (approximately An_{40}) occur in R887, R889, R897, R963, and in rock fragments in R897. Pyroxene and amphibole are unaltered. Sedimentary fragments are rare, only siltstone and limestone occurring.

Incipient metamorphism occurs in R888 and R894. In these rocks grain outlines are somewhat blurred by the growth of new minerals—sericite, epidote, prehnite, and probable pumpellyite—and the original textures of the volcanic fragments are no longer discernible.

DISCUSSION

Lithic Labile Arenites

Throughout the sequence these rocks are closely similar modally and petrographically. The dominant component is andesitic detritus—rock fragments, pyroxene, amphibole, iron oxides, and plagioclase, originally andesine-labradorite but now largely albitised. In addition there is usually a minor acid component of rhyolite and volcanic quartz. Not infrequently granitic detritus—plutonic quartz, orthoclase, and granite fragments—is present. A very minor sedimentary component is sometimes present and consists of autochthonous lutites or of allochthonous fragments which are termed subgraywackes and graywackes (or their siltstone equivalents) on textural grounds. These rocks are petrographically closely similar to graywacke-suite sediments occurring in the Middle and Lower Paleozoic terrain of central-western New South Wales.

The quartz in the lithic labile graywackes appears to be entirely of igneous origin. Globular fluid inclusions are abundant, and grains are usually unstrained. Keller and Littlefield (1950) consider that globular inclusions are characteristic of quartz of igneous rocks and gneiss. Unfortunately their study is not sufficiently extensive: they do not differentiate satisfactorily between volcanic and plutonic quartz, nor between the quartz of synchronous and subsequent granites, nor do they discuss the inclusions characteristic of vein quartz. The occurrence of occasional embayed grains and of grains with attached orthoclase suggests that both volcanic and plutonic quartz is present. This is confirmed by the occurrence of similar quartz as phenocrysts in rhyolite and in granite fragments, respectively.

The arenite units vary in frequency geographically and through time (Crook, 1959). This variation is probably attributable to variations in frequency and geographic distribution of tectonism peripheral to the trough and to the location of the mouths of submarine canyons.

These lithic labile arenites are similar to those described by Edwards (1950) from the Aure Trough, Papua, and by Edwards and Glaessner (1953) from the Wahgi Valley, New Guinea.

Polymictic Conglomerates

These appear to be related compositionally to the adjacent arenites and were presumably derived from the same source. They probably represent submarine slide deposits since they merge into pebbly mudstones, similar to those described by Crowell (1957).

Feldspathic Labile Arenites

As a group these contain more quartz than other types. The quartz, which may be embayed and contain fluid inclusions, is probably volcanic. The association of this with oligoclase-andesine, which is frequently subhedral, and devitrified pumice and glass

shards suggests that these arenites may be redeposited tuffs. In many cases there has been admixture of terriginous and autochthonous detritus—rock fragments and organic debris.

The association quartz, oligoclase-andesine, might suggest dacitic volcanism, but dacitic detritus does not appear in the lithic labile arenites. The feldspathic labile arenites may therefore be of mixed origin, the quartz and plagioclase coming from different sources.

Mudstones

For the most part these represent a mixture of pelagic and low competency turbidity current deposition (see Crook, 1959). Chlorite is probably dominant, and together with the albite is probably originally of andesitic origin. The quartz may be second cycle or igneous.

Argillaceous Limestones

The terriginous material in these rocks is very fine and is probably largely of andesitic origin. It is similar in composition to that in the mudstones. The calcite was probably deposited chemically during early diagenesis or perhaps halmyrolosis.

Lithographic Limestone

This is almost exclusively chemical, with very minor biogenic and terriginous components. It represents an interval during which negligible detritus was reaching large areas of the trough, for the Kiah Limestone is of considerable extent, having been traced 50 miles along the strike. The explanation for this hiatus in terriginous sedimentation is obscure. There is no change in the type of detritus or deposition above it, and in those places where the limestone is absent it is not possible to specify the equivalent horizon with any accuracy.

NATURE OF SOURCE AREA

The petrogenetic unity of the Parry Group sediments indicates a lithological similarity of source areas throughout the period of deposition. Like the upper parts of the underlying Tamworth Group, there is a strong andesitic component with a minor rhyolitic and plutonic component. This and the deep-water sedimentation throughout most of the period of deposition suggests a complex andesitic island arc. Towards the end of the Tournaisian the trough began to fill at a rate greater than its depression, and the water gradually shallowed. Subsequently (in the Visean) terrestrial conditions ensued.

The island arc contained some included older material as indicated by the granite and old sedimentary detritus. The rhyolitic component was apparently intermittent but increased in importance towards the end of the Tournaisian. The freshness of all the detritus suggests a brief predepositional history, and erosion was probably rapid in the source area.

ACKNOWLEDGEMENTS

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REFERENCES

Chayes, F., 1956, Petrographic modal analysis. John Wiley and Sons, Inc., New York, 113 p.

Crook, K. A. W., 1959, Lithotopic relationships in deep water troughs: Jour. Sedimentary Petrology, v. 29, p. 336–342.

———, 1960a, Classification of arenites: Am. Jour. Sci. v. 258, p. 419–428.

———, 1960b, Stratigraphy of the Parry Group (Upper Devonian-Lower Carboniferous), Tamworth-Nundle district, N.S.W.: Jour. Roy. Soc. New South Wales v. 94 (in press).

———, 1960c, Petrology of Tamworth Group, Lower and Middle Devonian, Tamworth-Nundle district, New South Wales: Jour. Sedimentary Petrology, v. 30, p. 353–369.

Crowell, J. C., 1957, Origin of pebbly mudstones: Geol. Soc. America Bull., v. 68, p. 993–1010.

Edwards, A. B., 1950, The petrology of the Miocene sediments of the Aure Trough, Papua: Proc. Roy. Soc. Victoria, v. 60, p. 123–148.

Edwards, A. B., and Glaessner, M. F., 1953, Mesozoic and Tertiary sediments from the Wahgi Valley, New Guinea: Proc. Roy. Soc. Victoria, v. 64, p. 93–112.

Keller, W. D., and Littlefield, R. F., 1950, Inclusions in the quartz of igneous and metamorphic rocks: Jour. Sedimentary Petrology, v. 20, p. 74–84.

Packham, G. H., 1954, Sedimentary structures as an important feature in the classification of sandstones: Am. Jour. Sci., v. 252, p. 466–476.

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FIGS. 1–14, DECEMBER, 1960

INTRODUCTION TO THE PETROLOGY OF THE OIL-SHALE GROUP LIMESTONES OF WEST LOTHIAN AND SOUTHERN FIFESHIRE, SCOTLAND[1]

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ABSTRACT

Five distinctive limestone micro-facies (oolitic, oolitoid, micro-conglomeratic, shelly, and nodular) are recognised, each of which may be present within one individual bed. They generally indicate shallow water, restricted lagoonal conditions inimical to organic life. Sometimes the conditions were modified, allowing organisms such as worms and ostracods to proliferate; rarely, a widespread linkage of adjacent lagoons allowed a more comprehensive fauna to develop. The limestones are invariably associated with shales into which they normally sharply grade.

INTRODUCTION

The Carboniferous Oil-Shale Group of the Midland Valley of Scotland attains a maximum thickness of approximately 5000 feet in the Lothians immediately to the west of Edinburgh; there it consists of a succession of sandstones, shales, marls, limestones, and tuffs. Of these rocks the sandstones and shales are dominant and between them form approximately 90 per cent of the succession whereas the limestones in any exposed section rarely exceed 3 or 4 percent.

The group as a whole has been the subject of more than a century's investigation but mainly from the stratigraphical, structural, and palaeontological viewpoints. The petrological aspects have been generally neglected with the exception of one detailed paper on the Houston Marl (Teall, 1925) and a series of brief descriptive notes on the Burdiehouse Limestone by Phemister (1956). Phemister recorded the textural variations and mineralogy of the limestone from several localities without attempting any inference as to the possible mode of origin. Despite this overall neglect, especially of the other limestones, both Geikie (1902) and Cadell (1925) soon recognised that the group was probably deposited under shallow water lagoonal and estuarine conditions. The validity of their inferences which have passed into subsequent palaeogeographical literature (MacGregor, 1931; Richey, 1935; George, 1958; Kennedy, 1958) is now amply confirmed at least in part by this new petrological work on the limestones.

This introductory study represents a small part of a wider petrological examination of the Scottish Oil-Shale Group sediments and has been restricted, in general, to an area around the shores of the Firth of Forth (fig. 1). The limestones have been selected from a four-mile wide belt extending from Granton in the east to Blackness in the west on the southern side, and on the northern side from a belt one to two miles wide extending from Kinghorn westwards to Rosyth.

Figure 1 indicates the generalised stratigraphical succession and horizons at which the limestones have been examined. The precise positioning of the limestones proved difficult in the lower part of the succession below the Burdiehouse Limestone because of the relative lack of detailed structural and stratigraphical information.

PETROLOGY OF THE LIMESTONES

General Lithology

Apart from their light grey to light brown colour, the most common characteristic of

[1] Manuscript received January 11, 1960.

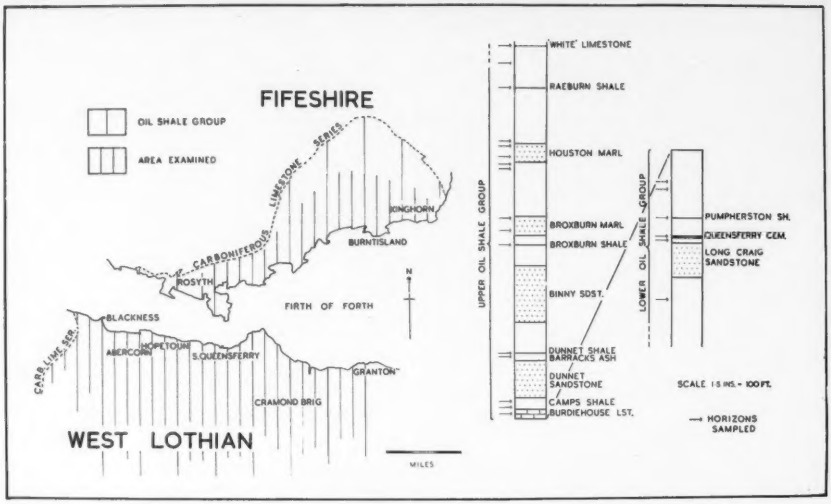

FIG. 1.—General geology of area studied.

the limestones in the field is their thinly bedded nature. The Barracks Ash limestones, for instance at Abercorn (British National Grid reference 081785) are approximately 6 in thick and lower group limestones to the west of Burntisland (221859) a mere 2 ft. The Burdiehouse Limestone is exceptionally thick, ranging between 5 and 48 feet although locally even this zone is separated by shales into three thin limestone beds 6 in to 2 ft in thickness, for example the Banks shore section (108788). It is also rather unusual in persisting over the entire Oil-Shale Group area whereas most of the others appear to wedge out when traced for any distance.

The limestones are invariably associated with shales, and there is little physical evidence of gradation between the two. This apparent sharp junction between the two lithologies often proves deceptive in that many of the interbedded shales are highly carbonate-rich. Likewise, many of the sandstones and marls within the succession have a high carbonate content although the former can never be seen *in the field* to grade into limestones. The physical gradation of shales into limestones is expressed more forcibly in rare places such as just above the Houston Coal zone in Craigton railway cutting (073766) by a progressive change from undisturbed shales below through limestone nodular bands into a continuous limestone bed above. The implication is more obviously of a gradual change in environmental conditions from muddy to relatively clearer waters than in the cases where a sharp lithological break is apparently present.

Many of the limestones exhibit polygonal cracking on their upper and lower surfaces which indicates either a shallow veneer of water or uplift above water level. Furthermore, tubes bored by shallow water organisms, possibly worms, are equally common. These can be well seen on the foreshore to the north of Hopetoun House (093792) in limestones approximately 80 ft below the Burdiehouse Limestone.

Secondary calcite and dolomite veining is very widespread in the beds as it is throughout the other associated lithologies.

Textures and Structures

The textures and structures of most of the limestones vary considerably not only from locality to locality but also at any one exposure. Indeed, within a single exposure an

individual bed may show well marked changes. These changes are, however, usually only seen in thin-section. The Burdiehouse Limestone, for instance, has been described by Phemister (1956) as a very fine grained (pelitomorphic) rock which is sometimes microconglomeratic (homiolithic), sometimes fossiliferous (clastizoic), and quite often silty (luteous) and bituminous. The present work also shows that to the east of Society (108788) ooliths up to 0.25 mm in diameter are present.

Oolitic and Oolitoid.—Oolitic texture is very common in all the limestones of the group, particularly in those beds below the Burdiehouse Limestone such as the Queensferry Cements and their approximate lateral equivalents (fig. 2A). The ooliths are rarely greater than 1 mm in maximum diameter and frequently show the characteristic internal concentric structure. At the Barracks Ash horizon southwest of Abercorn (081785), recrystallisation has partially destroyed the structures and brought about an overall textural homogenization of the rocks, but this is unusual.

The carbonate of the ooliths appears to be an Fe-rich dolomite ($\omega = 1.679$–1.683), and often they are set in a matrix of similar nature. It is the partial breakdown of this mineral to limonite during Recent weathering which gives many of the beds their familiar light brown surface appearance in the field.

The matrix minerals rarely form more than 50 percent of these beds and in addition to including carbonates also consist of carbonaceous matter, bituminous fragments, and angular clastic grains such as quartz, andesine, and hydrobiotite. In contrast to the Fe-rich dolomites of the matrix with their anhedral shape and grain size less than 0.02 mm, calcite ($\omega = 1.658$) and dolomite ($\omega = 1.680$) grains are larger and only locally dominant. It is very rare to find the coarse calcite euhedral, and it never shows a replacement relationship to any other mineral or structure. What does occasionally seem to

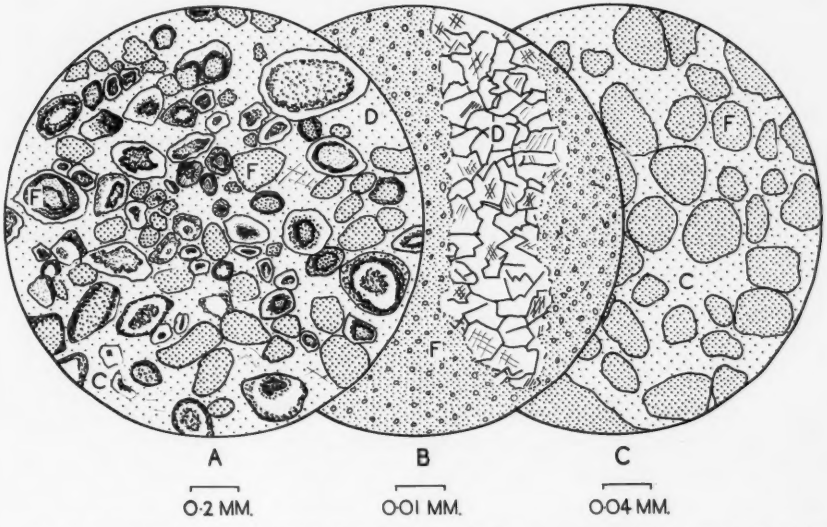

FIG. 2. A.—Oolitic texture. Partially limonitized Fe-rich dolomite (F) ooliths in a matrix of calcite (C) and dolomite (D). Limestone below Burdiehouse Limestone at Hopetoun. X nicols.
B.—Dolomite-infilled vugh. Queensferry Cements, Newton. X nicols.
C.—Oolitoid texture in "worm tube" limestone at Hopetoun. X nicols.
Note: In all the sections the density of stippling of the Fe-rich dolomite (F) indicates the degree of limonitization.

be replacement proves to be structural transgression caused by internal pressure-solution effects which produce micro-stylolites; the other varieties of limestone are similarly affected. Rather surprisingly, the evidence for dolomitisation is almost negligible and is expressed entirely in the form of irregularly shaped, small transgressive vugs up to 1.20×0.10 mm in size. These cavities are sporadically distributed, have a lining of coarse subhedral dolomite, and often have a subsequent infill of a kaolinite-like clay mineral. In thin-section the coarse clear dolomite is seen to grade into the Fe-rich dolomite grains of the matrix which suggests that it represents a localised solution and reprecipitation effect hardly akin to the wholesale metasomatic changes associated with true dolomitisation (fig. 2B).

Intimately intermingled with the ooliths in many of the limestones including the Burdiehouse Limestone at Hopetoun (093792) and Society (108788) are similar shaped and sized bodies to which the term oolitoid can be applied (fig. 2C). They lack the internal structure normally found in ooliths and consist of a fine grained aggregate of Fe-rich dolomite. It seems unlikely that they are recrystallised ooliths because that effect is uncommon; neither does a faecal origin appear feasible because organic remains may be absent from the limestone concerned. The probable answer to this problem rests within two previously mentioned limestone beds exposed on the eastern limb of the Hopetoun anticline. These beds are 18 in to 2 ft thick and occur within the Lower Group approximately 120–150 ft west of the Burdiehouse Limestone outcrop. When examined carefully at this locality they can be seen to be full of narrow, elongate tubes (0.50 mm average diameter×10–15 mm long), presumably resulting from the activities of organisms such as worms; cross-sections of these tubes are often observed in thin-sections. Furthermore, it is interesting to record that the abundance of worm tubes increases with the proportion of carbonaceous matter, which suggests that the organisms preferred a less pure environment for colonisation.

Breccias and Conglomerates.—A common internal feature of many of the limestones is micro- and macrobrecciation. Phemister (1956, p. 107) describes the rocks as homiolithic microbreccias although they have been variously described as desiccation breccias (Carruthers, 1912, p. 90) or desiccation conglomerates (Hyde, 1908, p. 400). The older terms are less satisfactory because of their genetic implication; in many cases the rounded nature of the limestone fragments would rather imply shallow water penecontemporaneous erosion.

The Queensferry Cements at Cramond Brig (173752) and South Queensferry (141784) are partially microbrecciated. At Cramond Brig the medium grey, subrounded to subangular fragments are up to 1 cm in maximum diameter and are set in a mottled darker grey matrix (fig. 3A). Both the fragments and matrix are composed of a fine grained aggregate of Fe-rich dolomite (grain size about 0.001 mm), but the matrix is more carbonaceous.

At South Queensferry the limestone bands vary in thickness from 1 to 6 in and are sometimes nodular. Within the bands there is often a poorly defined and irregular internal lamination parallel to the bedding which is primarily caused by fluctuations in the grain size of the carbonate. Additional emphasis is attained by the presence of opaque carbonaceous matter within the coarser laminae. It is the coarser layers which also contain subangular fragments derived from subjacent laminae presumably during phases of shallowing or stronger current action. The presence of sporadic clastic quartz grains (up to 0.60 mm diameter) intermingled with the fragments suggests that currents of greater carrying capacity and thus eroding power were probably more important than an actual shallowing of the waters.

The "White Limestone," a dense rock near the top of the succession and exposed on the foreshore to the west of Blackness (048804), is distinctively microbrecciated in part (fig. 3B). The subangular to rounded dark grey fragments measure up to 2.50 mm by 1.50 mm and are set in a finer grained, lighter grey carbonate matrix in which angular quartz and clay minerals are relatively abundant. The quartz, in fact, forms approximately 10 percent by volume of the brecciated layers, and this indicates even more agitated waters. It is a significant

trend which, moreover, is continued into parts of the Broxburn Marl horizon at Abercorn (082795) and Midhope Burn (078788) where a 20 to 40 percent clastic content is reached.

The most intensively micro- and macro-brecciated and conglomeratic limestones in the area belong to the Lower Group and are exposed to the west of Burntisland (221859). They have already been described in detail (Greensmith, 1959) and consist of approximately 6 ft of thoroughly broken up beds in which the debris has sometimes accumulated into mounds or lenticles. These mounds may have been partly stabilised by binding algal organisms of the *Ortonella* type. At this locality, as at most of the others, ooliths are present within the brecciated layers.

Shelly.—A rather remarkable feature of most of the limestones described above is the general absence of faunal content. A comprehensive fresh water fauna has been found locally in the Burdiehouse Limestone (Hibbert, 1836), and the widespread presence of worm tubes at other localities indicates that life was never entirely absent. On the other hand, as the textures and structures described so far suggest agitated, shallow, and thus presumably highly oxygenated waters, it is surprising that life should have been so restricted in the limestones. Possibly the salinity might have been such as to prohibit faunal proliferation and migration. Whatever the inhibiting factors, it is interesting to note that an input of carbonaceous and bituminous matter into the areas of carbonate precipitation seems to have modified conditions so that life could exist once more in quantity. Probably this organic matter was brought in by fresher waters from adjacent swampy areas and the actual breakdown of the matter itself may also have contributed to changes in the physico-chemical conditions.

All the varieties of shelly limestone produced by the new conditions are generally lacking in the presence of ooliths which may be a further indication of lower salinity in addition to suggesting quieter waters.

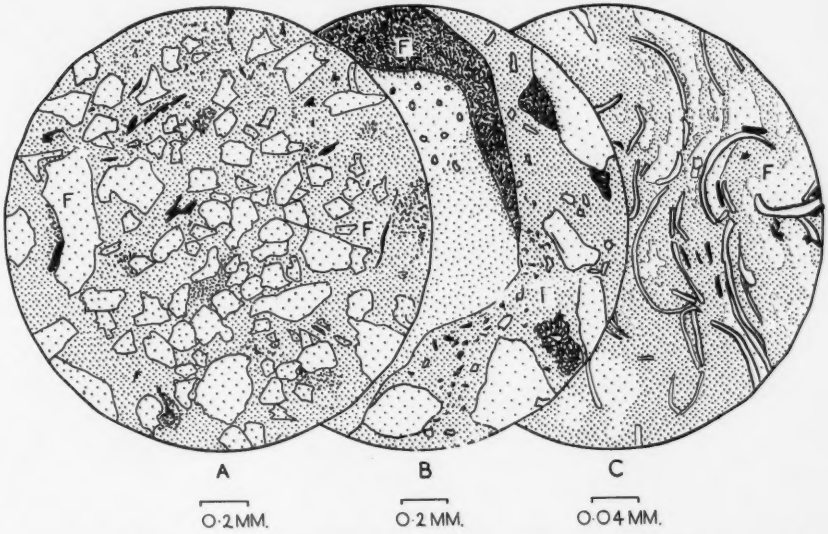

FIG. 3. A.—Microbrecciation in the Queensferry Cements near Cramond Brig. Local angular fragments set in a more carbonaceous matrix. X nicols.
B.—Microbrecciation in "White Limestone" near Blackness. X nicols.
C.—Shelly texture in Broxburn Marl limestone in Midhope Burn, Abercorn. Calcite shells in Fe-rich dolomite matrix. X nicols.

Good examples of these finely laminated, grey to black limestones are exposed at approximately the Burdiehouse Limestone level at Burntisland golf course (247868) and Hopetoun, the top of the Houston Marl and within the Broxburn Marl at Midhope, and near to the Raeburn Shale level east of Blackness (070793) (fig. 3C). All these beds are highly fossiliferous, and the fragmentary shells are normally preserved in coarse calcite. Coiled discoidal gastropods and lamellibranchs are present sometimes with crinoid debris coming in at higher levels in the succession. More abundant and widespread than any of these organisms are ostracods which are often packed tightly into microcoquinoid layers (Phemister, 1956). They are set in a matrix of fine to medium grained limonitized carbonate, golden to red-brown bituminous fragments, and black carbonaceous matter. Furthermore, the shells are usually disarticulated and partially contorted as a result of subsequent compaction although they are not abnormally comminuted. This substantiates the postulated lack of strong current action during their accumulation.

A common feature of these fossiliferous carbonaceous limestones is the presence of early diagenetic microspheroidal and nonspheroidal pyrite which replaces the calcite shells and the carbonate of the matrix. Their formation and the replacement reaction probably took place soon after burial because lenticular aggregates in the matrix sometimes show subsequent warping caused by compactive effects (fig. 4A). The origin of this early pyrite is conjectural but it may be associated with reducing conditions caused by the decomposition of carbonaceous matter and the activities of organisms such as *Pyritosphaera* and *Pyritella* (Love, 1957).

Lenticular and Nodular Bands.—The least conspicuous limestones in the Oil-Shale Group are dark grey to brown lenticular and nodular seams. These seams, present throughout the group, are thin (½ to 6 in).

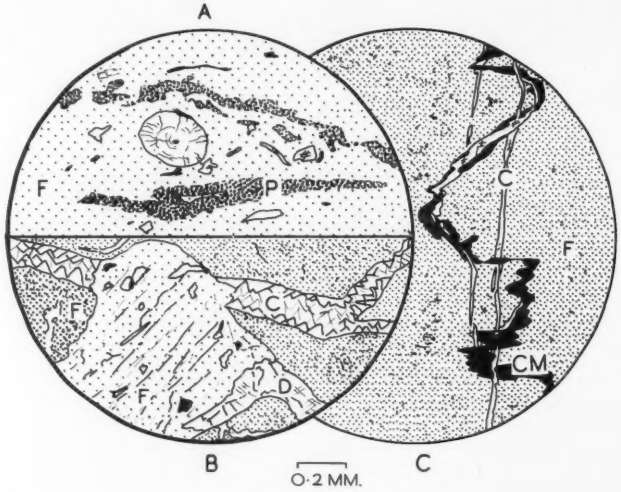

FIG. 4. A.—Early diagenetic pyrite (P) showing warping due to compaction. A crinoidal, shelly limestone near to the Raeburn Shale horizon to the east of Blackness. X nicols.

B.—Two generations of veining in a carbonate nodule at the Dunnet Shale horizon, Society. Early calcite (C) and dolomite (D) veins truncated by carbonate rich clastic vein. X nicols.

C.—Stylolite with concentrated carbonaceous matter (CM) in Fe-rich dolomite seam at Broxburn Shale horizon, Bridgend. Secondary calcite veins (C) transgress and follow the stylolitic seam. X nicols.

The composition is variable, generally siderite but sometimes fine-grained Fe-rich dolomite. Carbonaceous and bituminous matter together with pyrite are usually present.

Peculiarities noted at the margins of some of the nodules and seams are fractures, some of which are infilled with calcite and dolomite and others with clastic quartz and carbonaceous matter set in carbonates (fig. 4B). The time relationships of these two varieties of vein are generally obscure but at least in one instance, the Dunnet Shale, Society (098791), the clastic assemblage truncates the calcite-dolomite veins. If the clastic infill is an expression of the mobility of the surrounding shales, it seems likely that the actual process of infilling was early diagenetic although clearly preceded by the calcite-dolomite veining.

At other horizons, such as the Broxburn Shale near Bridgend (042761), stylolites are present which may be transgressed by carbonate veins (fig. 4C). On the assumption that these veins tend to be early diagenetic in origin, it can be tentatively concluded that the stylolites are also early diagenetic. Thus, they may have been generated while the limestone seams were still somewhat plastic and in their earliest phase of progressive dehydration and fracturing.

SUMMARY AND CONCLUSIONS

Although forming a low proportion of the total Oil-Shale Group sediments, it is clear that the varieties of limestone express distinctive phases (or microfacies) of sedimentation. These phases were generally characterised by shallow and possibly warm waters in which oolith formation, penecontemporaneous brecciation, and dehydration cracking were commonplace. Moreover, the conditions must have been such as to prohibit abundant life except during fresher water influxes. The broad pattern suggests, therefore, fresh to relatively highly saline lagoons (not necessarily marine) restricted in extent so as to effectively prevent faunal migration from adjacent and possibly more marine regions, particularly to the northeast. The migratory barriers between adjacent lagoons may have been physical in the form of mud and sand banks or physicochemical and thus related more to the prevailing bottom conditions and "sag and swell" structure of the basin floor; either possibility is feasible.

At certain stages of the lagoons' history it is doubtful if clear waters persisted for long and during the short time available only thin lenticular and nodular bands formed. As the waters progressively cleared, thicker and purer limestones were deposited, and in some instances this purification appears to have been accompanied by a lateral union of the lagoons into common and widespread basins of carbonate deposition. The Burdiehouse Limestone is the prime example of this short-lived unification.

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REFERENCES

CADELL, H. M., 1925, The rocks of West Lothian. Oliver and Boyd, Edinburgh, 390 p.

CARRUTHERS, R. G., 1912, The oil-shales of the Lothians: Scotland, Geol. Survey Memoir, 119 p.

GEIKIE, A., 1902, The geology of eastern Fife: Scotland Geol. Survey, Memoir, 421 p.

GEORGE, T. N., 1958, Lower Carboniferous palaeogeography of the British Isles: Yorkshire Geol. Soc. Proc., v. 31, p. 227–318.

GREENSMITH, J. T., 1959, An Algal Breccia-conglomeratic limestone in the Oil Shale Group, Burntisland, Fife: Geol. Soc. Glasgow Trans., v. 24, p. 14–18.

HIBBERT, S., 1836, On the fresh-water limestone of Burdiehouse in the neighbourhood of Edinburgh, belonging to the Carboniferous group of rocks: Royal Soc. Edinburgh Trans., v. 13, p. 169–191.

HYDE, J. E., 1908, Desiccation conglomerates in the Coal-measures limestone of Ohio: Am. Jour. Sci., v. 25, p. 400–408.

KENNEDY, W. Q., 1958, The tectonic evolution of the Midland Valley of Scotland: Glasgow Geol. Soc. Trans., v. 23, p. 106–133.

LOVE, L. G., 1957, Micro-organisms and the presence of syngenetic pyrite: Geol. Soc. London, Quart. Jour., v. 113, p. 429–437.

MACGREGOR, M., 1931, Scottish Carboniferous stratigraphy: an introduction to the study of the Carboniferous rocks of Scotland: Geol. Soc. Glasgow Trans., v. 18, p. 442–558.

PHEMISTER, J., 1956, The limestones of Scotland: petrography: Great Britain Geol. Survey Memoir, p. 66–139.

RICHEY, J. E., 1935, Areas of sedimentation of Lower Carboniferous age in the Midland Valley of Scotland: Geol. Survey, Summary Progress, Great Britain, v. 2, p. 93–110.

TEALL, J. J. H., 1925, Petrological notes on the Houston marl: with Chemical Analyses by E. G. Radley: Geol. Soc. Edinburgh Trans., v. 11, p. 327–337.

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FIGS. 1–6, DECEMBER, 1960

CROSS-BEDDING AND TEXTURAL VARIATIONS OF THE MIOCENE HAWTHORNE FORMATION IN NORTHERN FLORIDA[1]

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ABSTRACT

The Miocene Hawthorne Formation of northern Florida and southwestern Georgia consists principally of unconsolidated sands and thin beds of clay. It was studied to investigate the relationship between direction of cross-bedding and textural variations. From 24 outcrops 284 cross-bedding measurements were obtained and 50 size analyses were made.

In contrast to many other studies, cross-bedding of the Hawthorne Formation was found to be extremely variable but, nevertheless, indicating a southerly direction of transport with large local deviations. Toward the south the sands generally become coarser and have their poorest sorting. Relationships between sorting and the median diameter of the sands were not as clearly defined as in other studies.

Several possibilities are suggested to explain the anomalies in direction of transport and variation of texture.

INTRODUCTION

An investigation of the Hawthorne Formation in northwestern Florida and southwestern Georgia was undertaken in order to determine the relationship between direction of cross-bedding, median diameter, and sorting of the sand. From these relationships interpretation of the paleogeography was made.

DESCRIPTION OF AREA AND THE HAWTHORNE FORMATION

The area of this report lies within the outcrop belt of the Tertiary sediments in the Coastal Plain of the southeastern United States (fig. 1). The oldest formations (Cretaceous) crop out nearest the crystalline rocks of the Piedmont Province, and younger formations are encountered to the south.

The Hawthorne Formation crops out as a band of sand hills from the "panhandle" of Florida to South Carolina. This study was limited to the outcrop area between the Apalachicola River to the west and the Aucilla River to the east in Florida and northward to a line connecting Bainbridge and Thomasville, Georgia (fig. 2). To the south the Hawthorne Formation is either not present or is overlapped by Pleistocene sands. The Hawthorne Formation is considered to be middle Miocene in age, although recent work suggests a possible Pleistocene age for a portion of it (Pirkle, 1956, p. 232).

The lower part of the Hawthorne Formation in this area is a limestone with beds of sand and fuller's earth (clay mineral attapulgite). This unit is 20 to 60 feet thick and contains a middle Miocene fauna. The upper part consists of a maximum of 150 feet of sand with thin beds of clay. The sand is brightly colored, fine- to coarse-grained with some pebbles, friable to compact, and angular to rounded with the rounded grains commonly frosted. Many of the larger outcrops, within short distances, show vertical and horizontal variation in lithology. Generally, the sand bodies are wedge-shaped and many pinch out within distances of 10 to 20 feet. All of the outcrops of cross-bedding of the Hawthorne Formation were found in the upper sands.

METHODS OF STUDY

Samples of the upper sand were collected from 170 outcrops throughout the area of study. From these, 50 samples were chosen that produced complete areal coverage. Standard laboratory and statistical methods were used for the size analyses from which

[1] Manuscript received December 28, 1959.

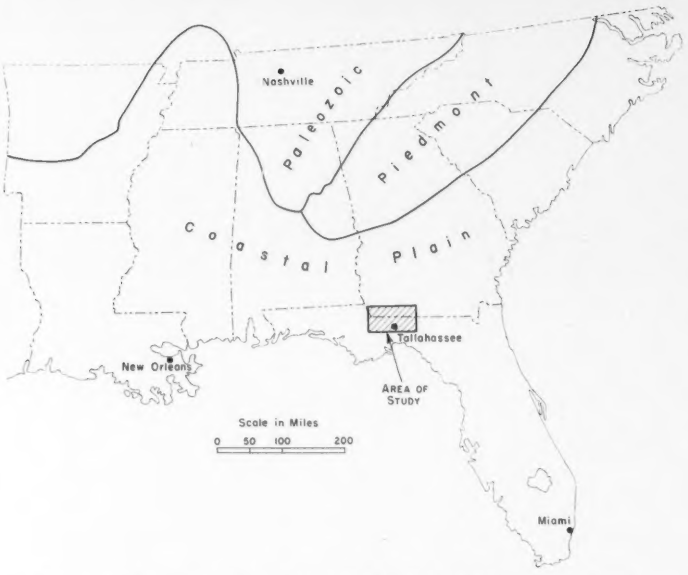

FIG. 1.—Index map of southeastern United States showing area of study.

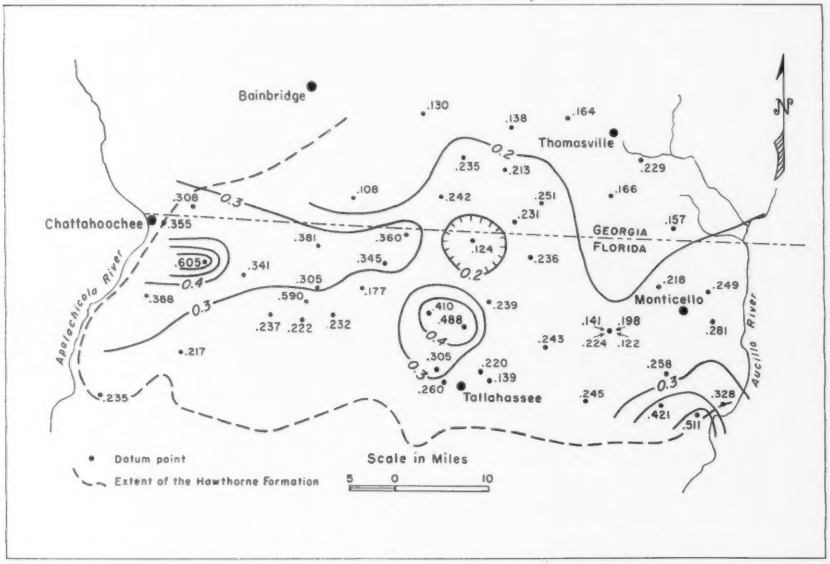

FIG. 2.—Median diameter of the sand grains of Hawthorne Formation.

the median diameter and the sorting coefficients of the sand were determined (figs. 2 and 3).

The cross-bedding in the Hawthorne Formation has been long recognized. Following the classification of McKee and Weir (1953, p. 385), the cross-bedding in the Hawthorne Formation is primarily of the planar type in which the lower bounding surfaces are planar surfaces of erosion. Commonly, the cross-bedded sedimentation units are up to 30 feet long and several feet thick. Dip of the foreset beds ranges between 10° and 15° but locally it is as high as 24°. When cross-bedding is treated statistically, it can be an important aid in reconstructing paleogeography.

At the 24 outcrops of cross-bedded sand, 284 measurements of the direction and amount of dip were made. Because of a paucity of cross-bedded sands in most outcrops, all possible observations were made at each outcrop. The sands were cut by a knife so that two vertical surfaces were exposed at right angles to each other—one showing the cross-bedding as horizontal lines, the other showing the true direction of inclination. Observations were made only on clearly discernible cross-bedding.

The data from the cross-bedding were treated with the Tukey chi-square test (Tukey, 1954; Harrison, 1957; Rusnak, 1957, p. 53–54; Potter and others, 1958, p. 1023) to determine the direction of preferred orientation. For this study, a 90 percent confidence interval was used. The resulting direction and the number of observations per outcrop were plotted (fig. 4). Solid arrows represent reliability of at least 90 percent and broken arrows represent reliability of less than 90 percent. A windrose of the 284 cross-bedding readings shows wide dispersion (fig. 4). When the total number of readings is treated with the Tukey test, the preferred direction is 176 degrees, which is significant at the 95 percent confidence level. Using this vectoral mean as the sample mean, the standard deviation is 85.9 degrees.

RESULTS

For each of the 50 sand samples analyzed,

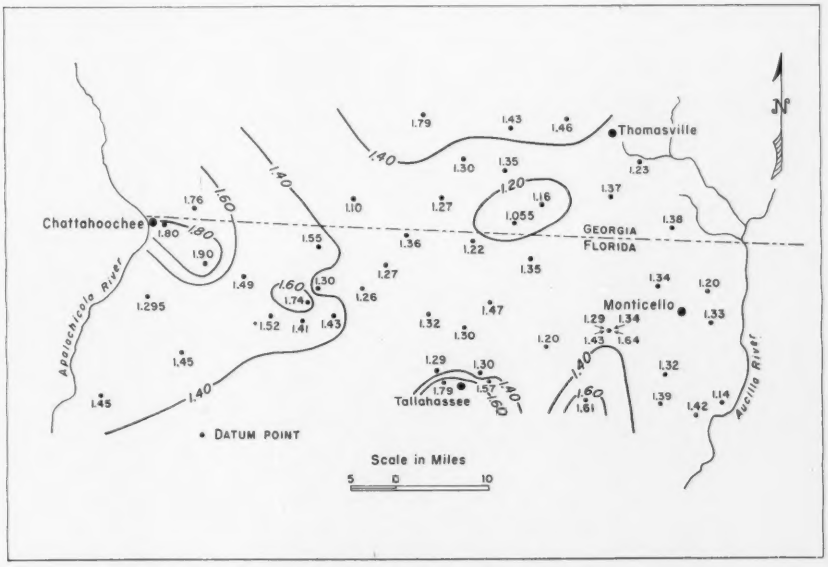

FIG. 3.—Coefficient of sorting of the sand grains of the Hawthorne Formation.

the coefficient of sorting and the median diameter were plotted together to determine their relationships. Inman (1949, p. 61; 1957, p. A1–A12) observed that a physical relationship exists between the coefficient of sorting and the median diameter of sediment samples. He found that sediments with median diameters near the size of fine sand (0.18 mm) are the best sorted whereas those that are either coarser or finer have higher sorting coefficient values. Sediments of the Hawthorne Formation, however, do not clearly show this relationship (fig. 5). The median diameter of sediments with the lowest coefficient of sorting is approximately 0.23 mm. Other sediments with approximately the same median diameter exhibit some of the highest values for sorting; therefore, no clear relationship is obvious between the median diameter and the coefficient of sorting in the Hawthorne sands.

The median diameter of the sand (fig. 2) increases from about 0.2 mm in the north to more than 0.4 mm in the south; it also increases from east to west but with several local deviations. The maximum median diameter (0.605 mm) of the sand grains occurs east of Chattahoochee, Florida. The sorting of the sand (fig. 3) also increases regionally from east to west and slightly to the south. Thus, the sands in the western part of the area are generally the coarsest and show the poorest sorting.

Cross-bedding in the Hawthorne Formation varies greatly among outcrops and shows very little consistency within the individual outcrop. Localized study of this cross-bedding, therefore, would lead to erroneous results. A windrose of all the observations (fig. 4) shows a general southerly direction of transport for the sediments with widespread deviation from the mean. A windrose of the cross-bedding means (fig. 6) also shows a direction of transport to the south with a secondary southwest-northeast direction of transport. These windroses differ greatly from those of most other cross-bedding studies which show one regionally dominant direction of sediment transport (Pettijohn, 1957, p. 475; Pelletier, 1958, plate 1; Pryor, in preparation, fig. 13).

A comparison of the direction of cross-

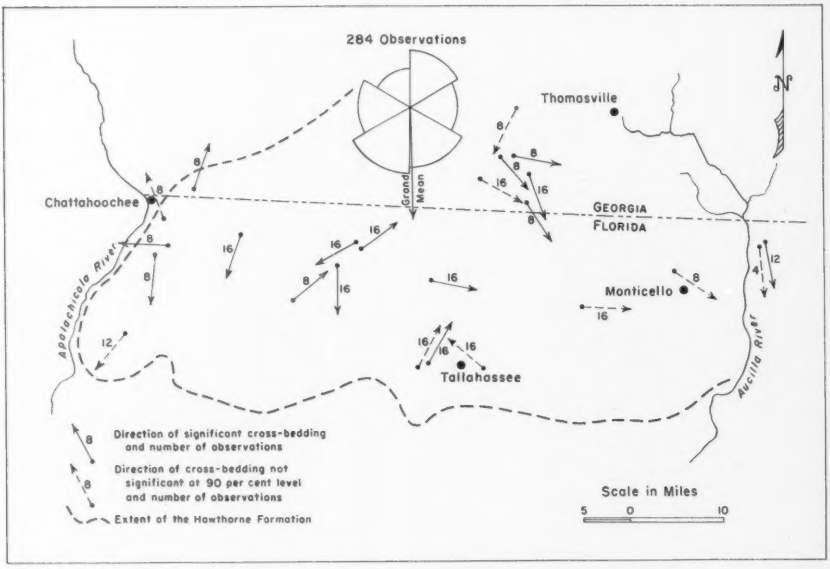

FIG. 4.—Direction of cross-bedding of the Hawthorne Formation.

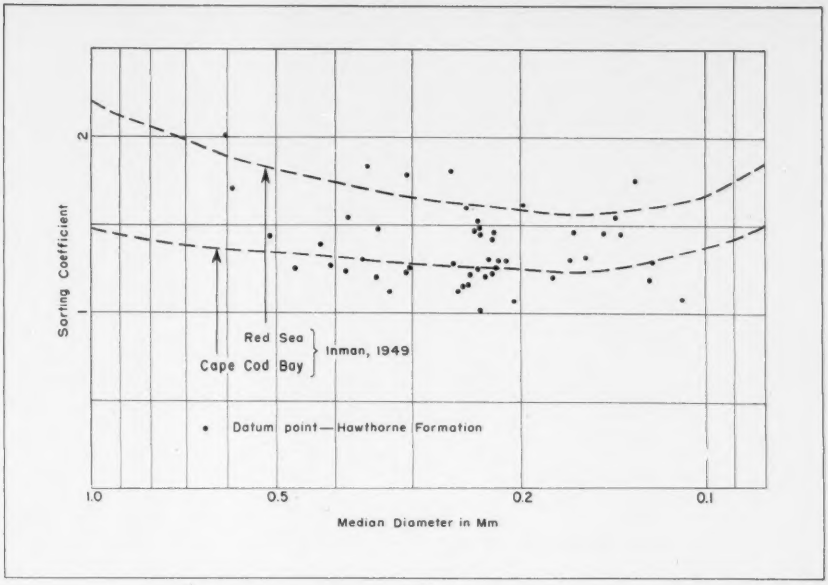

FIG. 5.—Relationship of coefficient of sorting and median diameter.

bedding and the median diameter of the sands (fig. 6) shows that although the overall regional direction of transport was toward the south, the median diameters of the sand grains increase from north to south. This is the opposite of what normally is expected in a simple fluvial dispersal system as indicated in studies by Russell and Taylor (1937, p. 237), Plumley (1948, p. 545), Potter (1955, p. 20), Schlee (1957, p. 1385–1388) and Pelletier (1958, p. 1053–1054), which show a decrease in grain size away from the source area.

INTERPRETATION AND SIGNIFICANCE

What can be inferred from the poorly developed regional pattern and wide variance of cross-bedding and the increase in grain size in the direction of sediment transport?

The increase in median diameter of sand grains toward the south, in the general direction of sediment transport, may reflect multiple environments. Finer grained sands may have been supplied from a northern source area whereas a secondary source of coarser grained sands lay west or northwest (note maximum median diameter around Chattahoochee, Florida, figs. 2 and 6). The areas of these coarser grained sands generally also exhibit the poorest sorting, possibly indicating less reworking.

Preferred orientation of cross-bedding is significant on the 90 percent level at only 16 of 24 outcrops (fig. 4), and the mean direction shows wide dispersion within small local areas. Windroses of the preferred orientation direction of each outcrop (fig. 6) and of the total number of cross-bedding observations (fig. 4) show a southerly direction of transport with strong diverging components.

Most previous studies of cross-bedding, such as those by Pettijohn (1957, p. 475); Pelletier (1958, plate 1); Potter and others (1958, fig. 15); and Pryor (in preparation, fig. 13) have shown one dominant regional direction of preferred orientation with only local variations. In the majority of these studies, it was possible to reconstruct the paleoslope. Study of the Hawthorne Formation cross-bedding shows only a very weak indication of direction of sediment trans-

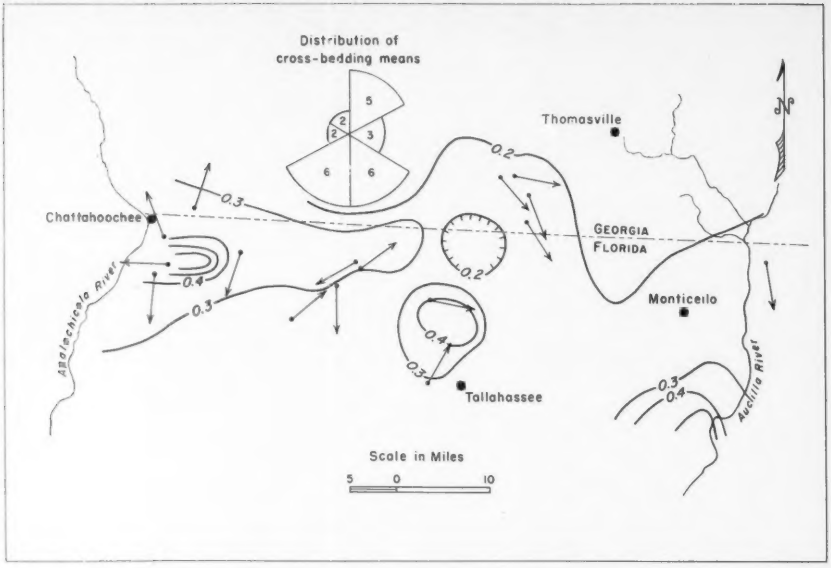

FIG. 6.—Direction of significant cross-bedding and median diameter of sand grains of the Hawthorne Formation.

port. Assuming that the deposition of Hawthorne sediments was dominantly fluvial implies a paleoslope dipping gently to the south. This interpretation would indicate that the variance of a fluvial disperal system may be related to the slope of the surface of deposition (Hamblin, 1958, p. 53; Pelletier, 1958, p. 1045–1046; Potter and others, 1958, p. 1041). The lower the gradient, the more variable the dispersion of a fluvial system. However, if the Hawthorne represents a shallow marine-shelf sand, as seems likely, this great variability might be readily explained by weaker, more variable marine-shelf currents.

A comparison of the median diameter and the significant cross-bedding of the sand (fig. 6) presents a complex pattern for reconstruction of the geography during deposition of Hawthorne sediments. The sands were deposited by currents flowing on a surface sloping toward the south. Locally, the currents deviated greatly from this southern direction and there probably were currents flowing in a northeast-southwest direction, possibly along shore, especially in the western half of the area of this study. The increase in median diameter of the sands from north to south and from east to west also supports the idea that additional coarser material was supplied from the west.

With these seemingly conflicting data it is difficult to determine the environment of deposition, but several possibilities can be eliminated. The poor orientation of cross-bedding and increasing median diameter of sand grains away from the source area does not fit the patterns developed in most deltaic or terrestrial deposits which commonly have well orientated cross-bedding.

In central Florida the Hawthorne Formation is primarily a sandy marine carbonate, indicating that marine conditions existed to the south. It, therefore, appears probable that the sediments of the Hawthorne Formation in northern Florida were brought in from north and west and were deposited in a near-shore area where weak and variable currents acted on them.

On the basis of these findings, it can be

seen that the Hawthorne Formation in northern Florida exhibits a series of sedimentary properties that do not conform with those generally reported. It is highly probable that other sediments occur that have some of the unusual properties of the Hawthorne.

ACKNOWLEDGMENTS

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REFERENCES

HAMBLIN, W. B., 1958, The Cambrian sandstones of northern Michigan: Michigan Geol. Survey Pub. 51, 146 p.

HARRISON, P. W., 1957, New techniques for three-dimensional fabric analysis of till and englacial debris containing particles from 3 to 40 millimeters: Jour. Geology, v. 65, p. 98–105.

INMAN, D. L., 1949, Sorting of sediments in the light of fluid mechanics: Jour. Sedimentary Petrology, v. 19, p. 51–70.

———, 1957, Wave-Generated ripples in nearshore sands: Department of the Army, Corps of Engineers, Tech. memo. no. 100, 65 p.

MCKEE, E. D., AND WEIR, G. W., 1953, Terminology for stratification and cross-stratification in sedimentary rocks: Geol. Soc. America Bull., v. 64, p. 381–389.

PELLETIER, B. R., 1958, Pocono paleocurrents in Pennsylvania and Maryland: Geol. Soc. America Bull., v. 69, p. 1033–1064.

PETTIJOHN, F. J., 1957, Paleocurrents of Lake Superior Precambrian quartzites: Geol. Soc. America Bull., v. 68, p. 469–480.

PIRKLE, E. C., 1956, The Hawthorne and Alachua Formations of Alachua County, Florida: Florida Acad. Sci. Quart. Jour., v. 19, p. 197–240.

PLUMLEY, W. J., 1948, Black Hills terrace gravels—A study of sediment transport: Jour. Geology, v. 56, p. 526–577.

POTTER, P. E., 1955, The petrology and origin of the Lafayette Gravel, Part 1—Mineralogy and Petrology: Jour. Geology, v. 63, p. 1–38.

POTTER, P. E., NOSOW, E., SMITH, N. M., SWANN, D. H., AND WALKER, F. H., 1958, Chester cross-bedding and sandstone trends in Illinois Basin: Am. Assoc. Petroleum Geologists Bull., v. 42, p. 1013–1046.

PRYOR, W. A., in preparation, Cretaceous Sedimentation in the Upper Mississippi Embayment.

RUSNAK, G. A., 1957, A fabric and petrology study of the Pleasantview Sandstone: Jour. Sedimentary Petrology, v. 27, p. 41–55.

RUSSELL, R. D., AND TAYLOR, R. E., 1937, Roundness and shape of Mississippi River sands: Jour. Geology, v. 45, p. 225–267.

SCHLEE, J., 1957, Upland gravels of southern Maryland: Geol. Soc. America Bull., v. 68, p. 1371–1410.

TUKEY, J. W., 1954, Chi-square test of orientation, comment no. 1-A: Earth Science Panel Review Group CSPS-ASA, unpublished communication.

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FIGS. 1–3, PLATES I-IV, DECEMBER, 1960

DIFFERENTIAL CEMENTATION IN THE TUSCARORA SANDSTONE[1]

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West Virginia University, Morgantown, West Virginia and Texaco, Inc., New Orleans, Louisiana

ABSTRACT

The Tuscarora Sandstone is generally tightly cemented with secondary quartz but locally the cement is irregularly distributed. Some beds have a banded appearance caused by alternating layers of tightly cemented and poorly cemented zones. Argillaceous material occurs in the poorly cemented bands and apparently inhibited the development of normal secondary growths. A lattice pattern results where cemented bands formed at right angles to bedding as well as parallel to bedding. The transverse bands may have been controlled by fractures inasmuch as they are parallel to fractures in the formatior. Uncemented lenses occur in some beds which are otherwise tightly cemented. Gas pockets apparently prevented complete cementation in these beds. Considerable primary clay was replaced by secondary quartz because clay is present in the uncemented lenses but is lacking in the cemented rock enclosing the lenses. Thick clay coatings on grains may prevent growth of secondary quartz. If pressure solution does not occur, considerable porosity is present where the grains are coated with clay.

INTRODUCTION

As part of his investigation of the factors controlling cementation, the senior author has sought areas where considerable variation in cementation occurred over the span of a few inches. It was hoped that study of these areas of differential cementation would shed special light on cementation processes since such factors as temperature, pressure, and composition of connate waters would be constant over a limited distance. The only areas of marked differential cementation were found in Silurian sandstones from northern Tennessee to central Pennsylvania. One of the best localities for study in this belt is in the Tuscarora Sandstone at Harmon Rock on North Fork Mountain along Route 33 in Pendleton County, West Virginia. Other favorable areas are in Highland County, Virginia, where the Tuscarora Sandstone crops out along Route 250 on Monterey Mountain, four miles west of Monterey and on Jack Mountain, 3.2 miles west of McDowell.

LITHOLOGY

The Tuscarora Sandstone in Pendleton County, West Virginia, and Highland County, Virginia, ranges in lithology from a nearly pure quartz sandstone to one with as much as 5 percent argillaceous material. The argillaceous material is sericite with probably some illite. The sandstone is fine to coarse grained and is commonly cross-bedded. Although most beds are tightly cemented, a few beds are friable and some uncemented patches occur in beds which are otherwise well cemented.

CEMENTATION

Except for overgrowths on a few zircon (pl. I, fig. 1) and tourmaline grains, the chief cement in the Tuscarora Sandstone is secondary quartz. In the sandstones which were initially clean, normal overgrowths completely filled pores except in some of the coarsest beds. No discontinuity occurred between the rims and detrital cores in most specimens so few significant quantitative measurements of the amount of secondary quartz could be obtained. A moderate number of the detrital grains were very turbid but had clear rims; therefore an estimate of the relative amounts of secondary quartz in different specimens could be determined by noting the size of the rims on the turbid grains.

The habit of secondary quartz in the clay-bearing beds is more variable. In some places the quartz completely replaced the clay and resembles the growths in clean sand. In other places the secondary quartz engulfed the clay instead of replacing it. The growths which engulfed clay consist of groups of tiny quartz prisms with parallel sheets of clay on the prism faces (pl. I, fig. 3). A growth cut parallel to the c-axis of the quartz is seen to

[1] Manuscript received January 25, 1960.

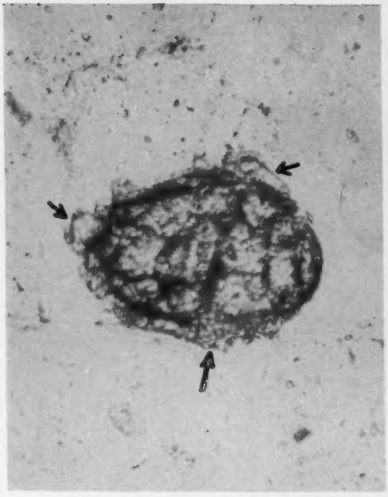

FIG. 1

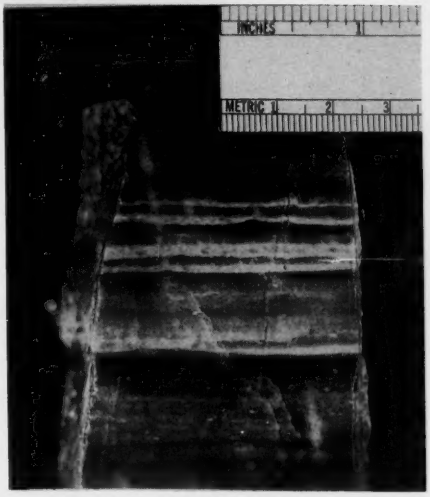

FIG. 2

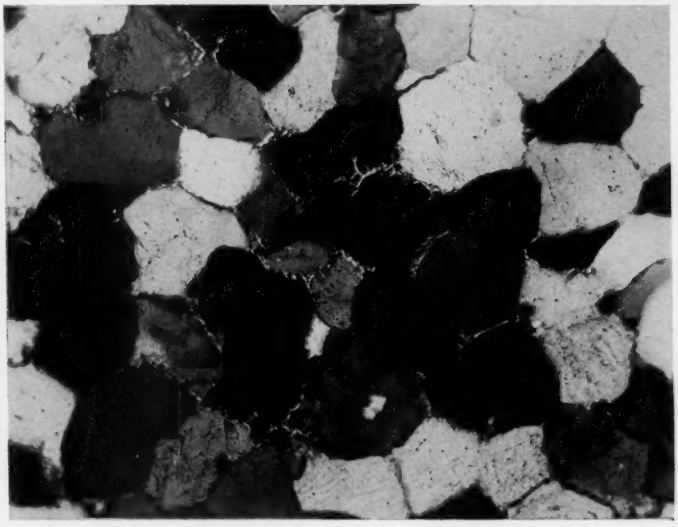

FIG. 3

PLATE I

FIG. 1.—Secondary growths (*arrows*) on zircon grain. Plain light, 205×.

FIG. 2.—Banding due to differential cementation. White bands are tightly cemented beds; dark bands are moderately argillaceous and nearly free of silica cement.

FIG. 3.—Intergrowths of secondary quartz and clay at grain margins. Crossed nicols, 90×.

consist of long slender prisms separated by films of clay with the same optical orientation. In sections cut perpendicular to the c-axis the clay inclusions tend to form a hexagonal grid as they outline the typical quartz cross-sections. In random sections the outlines also tend to be six-sided polygons but the lengths of the sides are unequal. The outer portions of some of the longer prisms are not in exact optical continuity with the rest of the grain. These growths can be easily mistaken for crushed grain margins or fine interstitial quartz of detrital origin.

Several factors appear to determine whether normal growths form with replacement of clay or whether prismatic intergrowths with clay develop. Random distribution of the two types of growths within a given specimen would seem to be caused by variations in the amount of clay coating on the grains. Small quantities of clay on one grain could be completely replaced whereas a thicker layer of clay on an adjacent grain might cause prismatic growths to form with intergrowths of clay. In some specimens, however, one portion of a bed will have normal quartz growths although another portion at the same horizon will have prismatic intergrowths with clay. As indicated in the section on differential cementation, it appears that the growths in these specimens formed in two stages with conditions favorable for complete replacement of clay limited to the first stage. Diagenetic changes in the clay may have rendered it more difficult to replace during the later period of cementation. Another possibility is that the composition of the later cementing solutions was less favorable for the breakdown of the clay lattices although the silica content may have remained fairly constant. Changes in temperature, rate of influx of the cementing material, and differences in concentration of silica may also have affected the degree of replacement of clay.

DIFFERENTIAL CEMENTATION

Some beds of the Tuscarora Sandstone are strikingly banded with alternating layers of tightly cemented sandstone and layers of argillaceous sandstone essentially free of cement (pl. I, fig. 2). The layers are normally only a few millimeters thick but are continuous for several tens of meters. Apparently, the original layers of clean sand became cemented whereas the clay in the argillaceous layers prevented secondary growth of quartz.

Another type of cementation yields a lattice pattern in which narrow bands of cemented sandstone occur perpendicular to bedding as well as parallel to bedding (pl. II, fig. 2). The cemented bands parallel to bedding are apparently the result of normal cementation of clean sand and are similar to those in the banded specimens. The transverse bands, however, cut across clay-bearing beds in which the clay coating on grains normally inhibits cementation. Furthermore, the cemented bands are free of clay except for the grains on the outer edges of the bands where the secondary growths characteristically contain small inclusions of clay. The fact that the growths are intergrown with clay at the margins of the cemented zones indicates that the clay was present before cementation. Inasmuch as abrupt changes in clay content along a given horizon were unlikely in the initial sand, the quartz cement must have completely replaced clay where the transverse bands cut across argillaceous beds. The fact that these bands are parallel to fractures in surrounding beds suggests that deformation may have been a controlling factor. Dislocations at certain zones may have produced more open packing of the sand grains and broken the clay coatings, thus facilitating the growth of secondary rims. Except for the transverse bands, most of the clay-bearing beds are free of cement; yet the clay content was not sufficient to make the beds impervious. It has generally been thought that secondary quartz was lacking in argillaceous sandstones because the tightness of the beds prevented entry of cementing solutions. However, the growths on zircon and tourmaline in many of the clay bearing beds in the Tuscarora Sandstone indicate that mineral bearing waters were available. This suggests that the clay coating on quartz grains rather than low permeability prevented the formation of normal quartz overgrowths. The present low permeability of these beds may have resulted from compaction after the period of cementation.

There are all gradations from the banded

FIG. 1

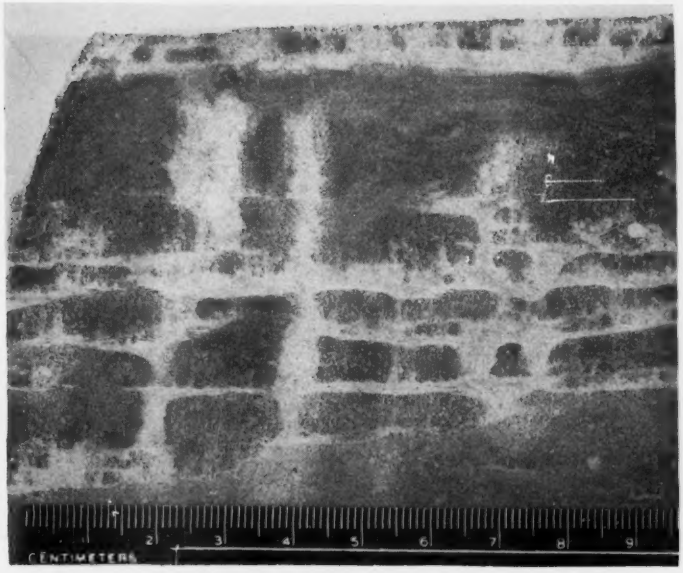

FIG. 2

PLATE II

FIG. 1.—Cemented projections extending upward from cemented bands. The base of each cemented band is sharp and appears to mark the base a graded bed.

FIG. 2.—Lattice pattern resulting from cementation along transverse bands as well along horizontal bands. Dark areas are clay-bearing and essentially free of silica cement.

type of cementation to the lattice type. In graded beds where clay content increases upward, the upper contacts of the cemented bands are irregular because of variations in clay which inhibited growth (pl. II, fig. 1). Long upward projections which taper out where the clay content is high occur apparently along dislocations which are similar to those which favored the development of transverse bands in the lattice type of cementation. These projections can be employed to determine the top of the beds as the projections consistently point upward from the original base of the beds.

Another conspicuous type of differential cementation involves uncemented or slightly cemented lenses within tightly cemented beds (pl. III, fig. 1). In the weathered outcrop the lenses are brown because of iron staining, whereas the enclosing rock is white. The lenses are essentially disk-shaped and range from a fraction of an inch to several feet across with a thickness of about one-tenth the width. The lenses were originally horizontal for they are consistently parallel to the major bedding planes. Inasmuch as they cut across cross-laminations (fig. 1), their formation was not controlled by primary features. Apparently pockets of gas prevented waters from completely cementing the beds during the main period of cementation. The former presence of gas is indicated by the bubble-like shape of the lenses and the fact that the lenses were horizontal originally regardless of laminations within the beds. The bases of the lenses are irregular where cementation advanced upward into the gas occupied areas but the tops of the lenses are smooth and the contacts with the cemented rock above are sharp. (pl. III, fig. 2).

Some lenses are very porous but others have clay-bearing prismatic growths which apparently formed during a later period of cementation. The lenses contain moderate amounts of clay but the enclosing cemented sand if free of clay except for grains at the margins of the lenses. Presumably clay out-

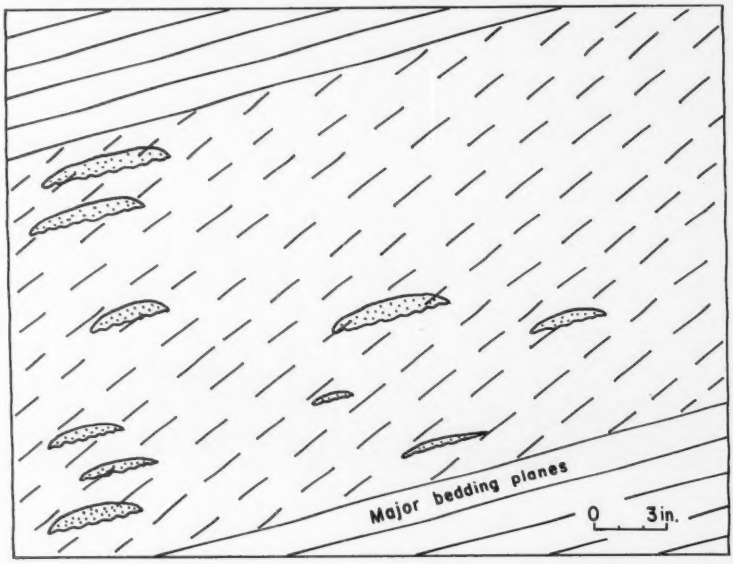

FIG. 1.—Uncemented lenses (stippled) within well-cemented cross-laminated bed. The lenses represent original gas pockets which prevented complete cementation of the bed. The lenses cut across the cross-laminations but are parallel to major bedding which was apparently horizontal when cementation occurred.

FIG. 1

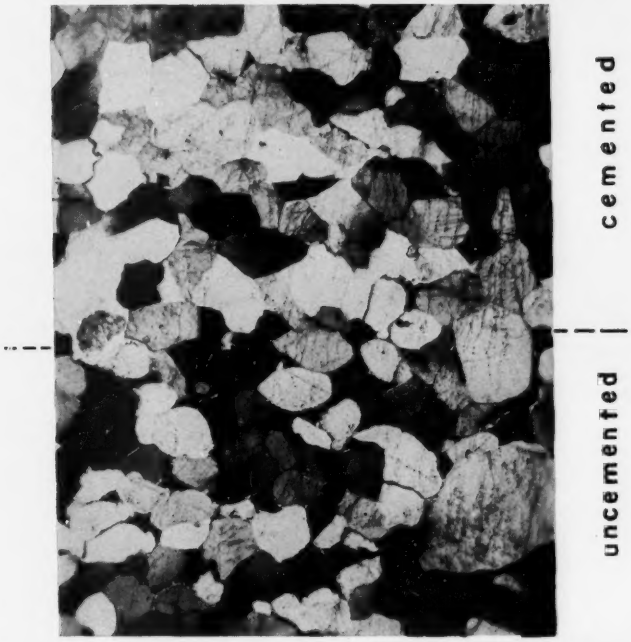

FIG. 2

PLATE III

FIG. 1.—Uncemented lens (*dark*) within a tightly cemented bed. Gas originally in the lens apparently prevented complete cementation.

FIG. 2.—Contact between an uncemented lens and tightly cemented sand above. Crossed nicols, 30×.

side the lenses was completely replaced. Since many of the lens-bearing beds are almost completely cemented, large quantities of clay must have been replaced. This means that a cemented sand which is now clean may actually have been clay-bearing initially.

In some beds there are uncemented patches over pebbles and clay galls which have the shape of a cone (fig. 2; pl. IV, fig. 1). The axes of the cones are always perpendicular to major bedding even in cross-laminated beds. These cones can be used in determining the tops of beds as the apices point to the original top. The origin of these uncemented cones is not known. It is unlikely that a single gas bubble would have had the shape of a cone originally or would cling to the upper surface of a pebble. O. L. Haught of the West Virginia Geological Survey has suggested that earthquake waves might initiate upward flow of water containing small gas bubbles. Bubbles that happened to move into the lee side of the pebbles might remain there because of the relatively quiet water at these points. If the bubbles remained until cementation was completed, they would keep cementing solutions from these areas and account for the uncemented cones.

PRESSURE SOLUTION

Some pressure solution occurred at the contacts of detrital grains in all rock types but was much greater in the clay-bearing beds. The effect of clay on pressure solution has been noted in several investigations (Heald, 1956; Thomson, 1959; Weyl, 1959). Pressure solution is least in the cemented beds apparently because of the lack of clay although restricted circulation and large contact areas may have been contributing factors. In clay-bearing lenses within cemented beds, stress at grain contacts apparently was not sufficient to produce appreciable solution because the enclosing rock bore the load. Similarly the lack of significant pressure solution in clay-bearing beds with transversely cemented bands appears to be caused by the fact that the bands supported most of the weight of the overlying beds.

In some specimens more compaction has occurred through pressure solution in the fine grained layers than in the coarse grained layers even though clay appears to have been fairly evenly distributed throughout the whole specimen. Commonly porosity is eliminated in the fine grained layers whereas appreciable porosity remains in the coarse layers. Apparently solution was greater in the fine grained layers because more contacts were present and the atoms had a shorter distance to travel along the smaller contact areas between grains.

In addition to pressure solution at grain contacts within beds, considerable solution occurred along stylolite seams. The seams

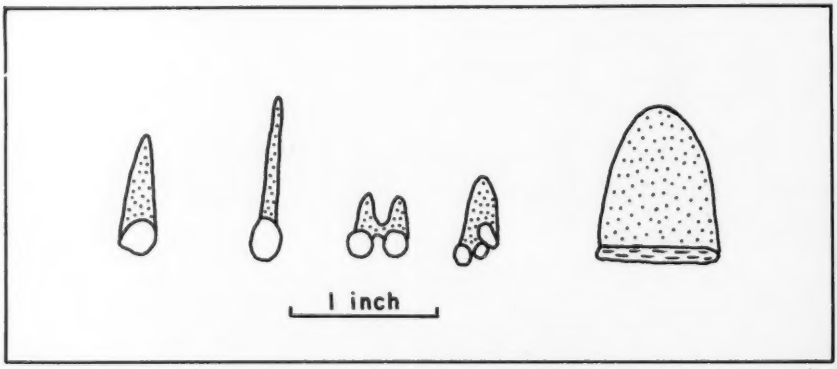

FIG. 2.—Sketches of typical uncemented patches (*stippled*) above pebbles and shale flake (*dashed*) within well-cemented bed.

FIG. 1

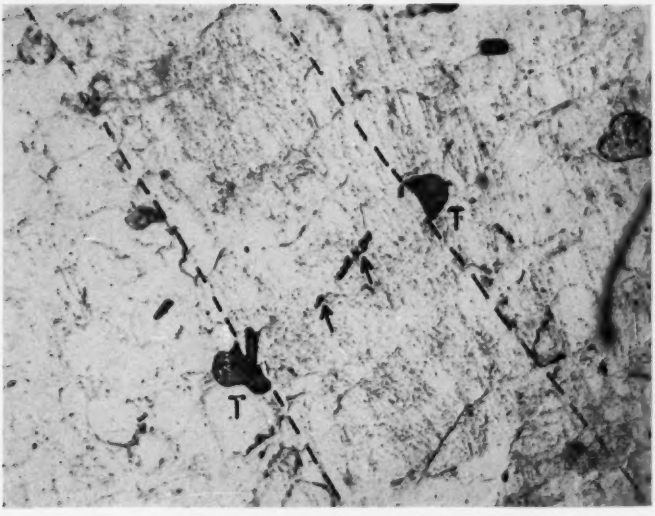

FIG. 2

PLATE IV

FIG. 1.—Uncemented cones (*dark areas*) over pebbles within cemented bed.

FIG. 2.—Quartz vein along fracture which cut tourmaline grain. Small tourmaline fragments (*arrows*) occur within the vein between the two halves (T) of the grain which are at the borders of the vein. Plain light, 60×.

are well developed and occur along most major bedding planes (Heald, 1955).

TIME OF CEMENTATION

The cementation apparently occurred after considerable burial because the sands are well compacted; yet the secondary growths have not undergone appreciable pressure solution. Most of the cementation preceded deformation because secondary growths are truncated by stylolite seams which formed before folding. Furthermore, the orientation of the lenses which were filled with gas indicates that most of the cementation preceded folding. Until the time of cementation, gas would have been free to move; hence the lenticular gas pockets would have remained horizontal regardless of tilting of the beds. Inasmuch as the lenses are now parallel to major bedding even on the flanks of folds, cementation must have occurred before folding while the beds were horizontal. This precluded the possibility of gas or oil migrating to structural highs to prevent cementation at these points.

CONDITIONS FAVORABLE FOR POROSITY

The Tuscarora Sandstone is characteristically tightly cemented and devoid of interstitial porosity. However, some thin, coarse grained beds are moderately porous whereas the adjacent finer grained beds are tight. In some places this difference is caused by greater compaction through pressure solution in the finer grained beds than in the coarse grained beds. Where secondary quartz is present, it is not clear whether the differences in porosity are caused only by differences in compaction or whether more secondary quartz was deposited in the finer layers. Dust rings were not sufficiently distinct for significant quantitative measurements of secondary quartz.

In the few differentially cemented beds some porosity exists where special conditions prevailed. The lenses which were occupied by gas during the main stage of cementation are generally porous although some have lost porosity through later cementation. The lenses have only limited reservoir possibilities because they are small in size and are separated by tightly cemented rock although some lenses are connected by channelways along late fractures.

In many of the beds with the lattice type cementation, some porosity exists between the transversely cemented bands. Two factors were important in preserving interstitial porosity in these beds. One factor was the coating of clay on the grains which inhibited the deposition of secondary quartz. In the surrounding beds of clean sandstone porosity was eliminated by the deposition of secondary quartz. The second factor was the supporting effect of the transverse bands which acted as pillars or walls and prevented complete compaction of the beds. Some compaction did occur where the transverse bands were pressolved into overlying beds with compensating pressure solution occurring at grain contacts in the layers between the bands (fig. 3), but porosity was not entirely eliminated. In the normal clay-bearing beds, compaction through pressure solution virtually eliminated the pore spaces except in the coarsest beds.

The Tuscarora Sandstone has been considerably fractured but most openings along

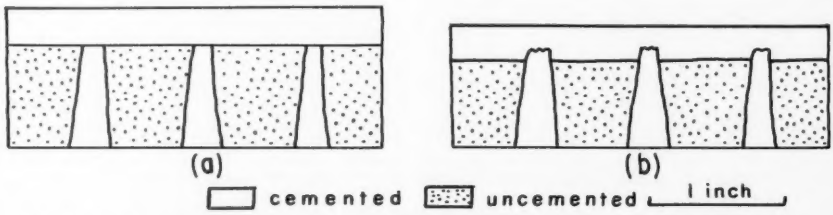

FIG. 3.—Bed with cemented transverse bands before (a) and after (b) pressure solution. Solution occurred at grain contacts throughout the uncemented portions of the bed and at the interface at the top of the transverse bands. The supporting effect of the bands prevented complete loss of porosity in the uncemented portions.

the fractures have been filled with quartz. Commonly the fractures are 0.1 mm apart and are marked by a series of liquid inclusions. Along some fractures there are veins up to 0.5 cm in width in which the vein filling is in optical continuity with the bordering quartz grains. A thin section of one of the fractured zones showed a vein cutting a tourmaline grain with fragments of tourmaline extending across the vein between the two halves of the grain which remained in the walls bordering the fracture (pl. IV, fig. 2). Apparently quartz deposition occurred nearly simultaneously with the opening up of the fracture so the fragments shifted only slightly instead of falling into an open fissure. Under these conditions openings would never have been large regardless of the presently observed distance between the original walls of the fractures. However, some secondary porosity occurs along later fractures where quartz filling is incomplete. The development of porosity along fractures was therefore governed in large part by the amount of secondary silica available rather than simply by the magnitude of the wall separation.

CONCLUSIONS

The study of differentially cemented sandstones has shown that the replacement of clay by secondary quartz may lead to erroneous conclusions as to the original clay content of sandstones.

It has been demonstrated that gas can prevent cementation although in the areas studied no large porous zones resulted. Where cementation preceded folding, the distribution of gas pockets was controlled by early sedimentary conditions rather than by later structural features.

Clay coating prevented cementation in some beds and if pressure solution had not occurred, porosity would have been high. This suggests that in areas where conditions were unfavorable for pressure solution, the beds with the most porosity would be those in which quartz grains were coated with clay.

ACKNOWLEDGEMENTS

The initial investigation of this problem was supported by project grant G-98 from the National Science Foundation, to which the writers wish to express their gratitude.

REFERENCES

HEALD, M. T., 1955, Stylolites in sandstones: Jour. Geology, v. 63, p. 101–114.

———, 1956, Cementation of Simpson and St. Peter Sandstones in parts of Oklahoma, Arkansas, and Missouri: Jour. Geology, v. 64, p. 16–30.

THOMSON, A. F., 1959, Pressure solution and porosity: Soc. Econ. Paleontologists and Mineralogists, Spec. Publ., No. 7, p. 92–110.

WEYL, P. K., 1959, Pressure solution and the force of crystallization—a phenomenological theory: Jour. Geophysical Research, v. 64, p. 2001–2025.

JOURNAL OF SEDIMENTARY PETROLOGY, VOL. 30, NO. 4, PP. 578–581.
FIGS. 1–3, DECEMBER, 1960

MINERALS ASSOCIATED WITH LOWER PENNSYLVANIAN CONGLOMERATE, LAWRENCE COUNTY, INDIANA[1]

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Indiana Geological Survey

ABSTRACT

Hydrated and dehydrated halloysite, allophane, crandallite, gibbsite, kaolinite, iron oxides, manganese wad, and barite are associated with quartz conglomerate of the early Pennsylvanian Mansfield Formation in southwestern Lawrence County, Indiana. Halloysite is found as lenses in the conglomerate and as rounded particles as large as pebble size. Allophane is found in lenses and exhibits columnar and botryoidal structures. Crandallite has formed at the expense of allophane. Manganese wad is found both as coatings on quartz pebbles and as pebble-free lenses as much as 6 inches thick. Most lenses of wad contain gibbsite and hydrated halloysite. Kaolinite occurs as rounded pebbles and as irregular particles between quartz pebbles. Iron oxides appear as irregular bands and stainings throughout the conglomerate. Two layers of well crystallized barite, each half an inch thick, are found about 200 yards southwest of the quarries at the contact of a Mississippian limestone and overlying red clay and quartz pebble residuum.

INTRODUCTION

Geologic setting

The basal part of the early Pennsylvanian Mansfield Formation in southwestern Indiana consists in places of a poorly consolidated quartz pebble conglomerate. Halloysite, allophane, and other minerals (Logan, 1922; Ross and Kerr, 1934) are associated with this conglomeratic phase of the Mansfield and appear to be concentrated near the Mississippian-Pennsylvanian unconformity. The most widely known occurrence of minerals associated with this conglomerate is the deposit at Gardner Mine Ridge (Callaghan, 1948). The purpose of this paper is to describe a similar occurrence of minerals associated with this conglomerate.

Location

A concentration of several mineral species recently has been observed in two abandoned conglomerate quarries in the Mansfield Formation about 3½ miles northwest of the Gardner Mine locality. Three quarries are located a few hundred yards north of the railroad bridge on State Road 450 west of Williams, Lawrence County, Indiana (fig. 1). The quarries, which are overgrown with weeds and small trees, are reached by partly overgrown wagon trails. The lower 5 ft of the quarry faces are covered with quartz pebbles loosened from the conglomerate above. The upper parts of the quarry walls, however, are clean and easily accessible and consist dominantly of a conglomerate composed of quartz pebbles in a matrix composed of clay size particles. The quarry closest to the road is a shallow pit about 125 feet long, 50 feet wide, and 10 feet deep. The middle quarry is about 60 feet long by 40 feet wide, and the quarry farthest from the road is about 75 feet long by 65 feet wide. The minerals described in this paper were found only in the latter two quarries, each of which has an exposed vertical face of 20 to 30 feet.

Minerals associated with the conglomerate

Hydrated and dehydrated halloysite are crystalline members of the kaolin group of clay minerals. The former has a basal spacing of about 10.1 Å, and the latter has a basal spacing of about 7.6 Å. The theoretical formula for hydrated halloysite is $(OH)_8Si_4Al_4O_{10}\cdot 4H_2O$; the theoretical formula for dehydrated halloysite is $(OH)_8Si_4Al_4O_{10}$. Most hydrated halloysite, however, contains between 3 and $4H_2O$, and dehydrated halloysite contains as much as $2H_2O$. Allophane is an amorphous hydrated alumino-silicate mineral, and crandallite, also known as pseudowavellite (Palache,

[1] Published with the permission of the State Geologist, Geological Survey, Indiana Department of Conservation, Bloomington, Ind. Manuscript received January 25, 1960.

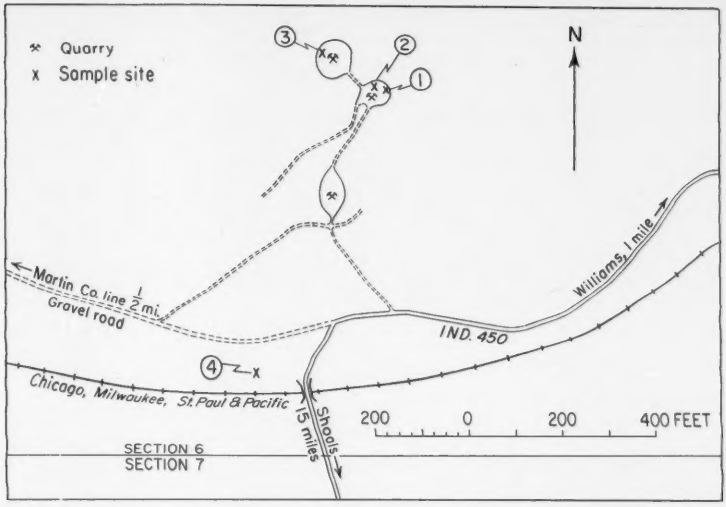


FIG. 1.—Sketch map showing location of quarries and sample sites near Williams, Indiana.

Berman, and Frondel, 1951, p. 837), has the formula $CaAl_3(PO_4)_2(OH)_5H_2O$. In addition to these minerals, kaolinite, $(OH)_8Si_4Al_4O_{10}$, gibbsite, $Al(OH)_3$, and wad (hydrous manganese oxides) are present in the quarries. Barite, $BaSO_4$, is present in a railroad cut a few hundred yards southwest of the quarries.

Previous work

The only previous mention of such minerals from these quarries is the report by Malott (1951, p. 245) that "some redeposited iron-stained clay derived from the pre-Mansfield clay residue of the Beaver Bend limestone occurs in the base of the Mansfield in the quarry pits, along with some fragments of redeposited white kaolin." Erd (1954, p. 31) noted that barite was present in the railroad cut near the pits, but he did not give a specific location for its occurrence.

MINERAL OCCURRENCE

A layer 6-in thick and at least 15 ft long, consisting dominantly of black wad, lies 5 ft above the quarry floor in the east wall of the middle quarry (site 1 of fig. 1). In addition to wad this layer also possesses randomly scattered white to brown areas which are composed essentially of hydrated halloysite; dehydrated halloysite and gibbsite are minor constituents of these areas. The layer contains no quartz pebbles. The conglomerate that is found above this layer contains very few wad stains, but the conglomerate below the layer contains abundant stains. A few pebbles of kaolinite and a few pebbles of dehydrated halloysite appear in the conglomerate above the 6-in layer. These probably are the "white kaolin" fragments mentioned by Malott (1951, p. 245).

In the north wall of the same pit (site 2 of fig. 1 and fig. 2) kaolinite is found in a 3-ft zone about 5 ft above the quarry floor as small, irregular, interstitial masses between quartz pebbles. Some angular pebbles of dehydrated halloysite also are found in this zone. Above this kaolinitic zone is a $2\frac{1}{2}$-in layer of sooty black wad which has compact dark-gray coatings of gibbsite. The wad layer contains no quartz pebbles. It can be traced horizontally for a distance of about 6 ft. About 10 ft of conglomerate lies directly above the wad. Many of the quartz pebbles of the conglomerate above the wad are stained with a thin coating of wad. Small white pebbles of kaolinite and dehydrated

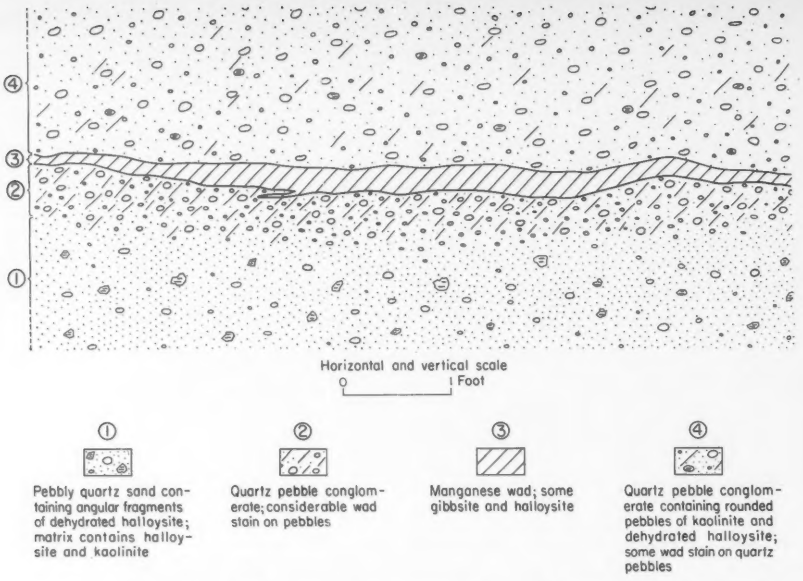
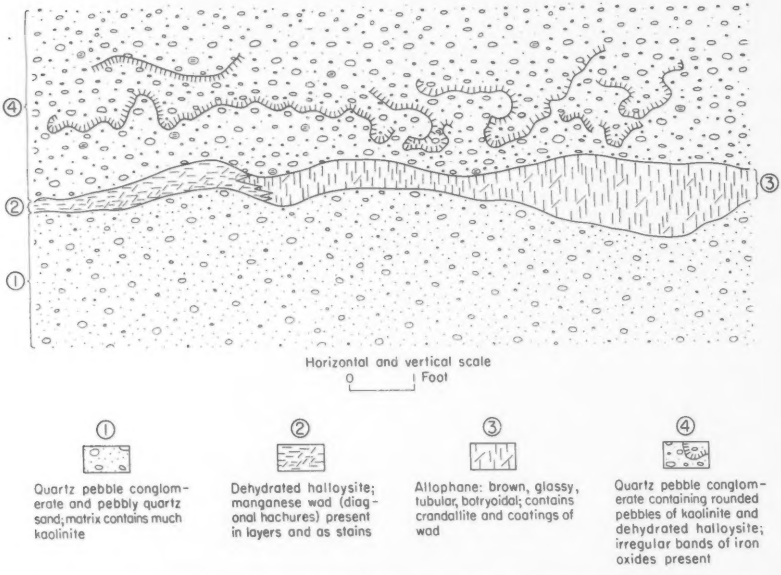

④
③
②
①
Horizontal and vertical scale
0
1 Foot
①
Pebbly quartz sand containing angular fragments of dehydrated halloysite; matrix contains halloysite and kaolinite
②
Quartz pebble conglomerate; considerable wad stain on pebbles
③
Manganese wad; some gibbsite and halloysite
④
Quartz pebble conglomerate containing rounded pebbles of kaolinite and dehydrated halloysite; some wad stain on quartz pebbles

FIG. 2.—Quarry face showing wad layer in quartz pebble conglomerate (site 2 of fig. 1).


④
③
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①
Horizontal and vertical scale
0
1 Foot
①
Quartz pebble conglomerate and pebbly quartz sand; matrix contains much kaolinite
②
Dehydrated halloysite; manganese wad (diagonal hachures) present in layers and as stains
③
Allophane: brown, glassy, tubular, botryoidal; contains crandallite and coatings of wad
④
Quartz pebble conglomerate containing rounded pebbles of kaolinite and dehydrated halloysite; irregular bands of iron oxides present

FIG. 3.—Quarry face showing halloysite and allophane layer in quartz pebble conglomerate (site 3 of fig. 1).

halloysite are scattered throughout this conglomerate.

In the west wall of the pit farthest from the road (site 3 of fig. 1 and fig. 3), flecks of kaolinite are interspersed in a 3-ft zone of conglomerate 5 ft above the quarry floor. Above this is a 1-ft layer of dehydrated halloysite, allophane, crandallite, and wad. The minerals of this layer contain no quartz pebbles and are present as lenses which thicken and thin and grade into each other horizontally. The layer extends at least 20 ft along the face of the pit. The allophane is glassy and possesses botryoidal and columnar structures when fresh. Crandallite, which is intimately associated with the allophane, appears as radiating crystals that seldom exceed 0.05 mm in their maximum dimension. Above this 1-ft layer is about 15 ft of conglomerate which contains pebbles of kaolinite and dehydrated halloysite. The kaolinite of these pebbles is in the form of elongated crystals as much as 0.06 mm long. These crystals are attached along their long dimension to form accordion-like bodies. A considerable amount of iron oxide is found in this conglomerate as irregular 1-in bands and as multicolored stains on quartz pebbles.

A railroad cut exposes shales and limestones of Mississippian age about 200 yards southwest of the quarries (site 4 of fig. 1). Unconsolidated quartz pebbles in a matrix of red-brown clay overlie a Mississippian limestone at the top of the cut. Immediately above the limestone, however, are two half-inch layers of blue-gray barite that are separated from each other by a half-inch layer of red-brown iron oxides. The long dimensions of the individual barite crystals are perpendicular to the bounding surfaces of the layers. Loose chunks of barite are strewn on the upper surface of the limestone on both sides of the railroad cut. Thus the barite layers probably once were continuous over a distance of at least 50 ft. The barite layers may extend beneath the conglomerate at the quarries.

DISCUSSION

Originally the halloysite in the quarries very likely was hydrated. Dehydration due to contact with the atmosphere, however, has caused much of the halloysite to change to the dehydrated variety. The pebbles of dehydrated halloysite probably were formed by reworking and dehydration of the hydrated halloysite that occurs below these pebbles. The pebbles of kaolinite, which are found in the same places as the pebbles of dehydrated halloysite, originally may have been halloysite pebbles; subsequent reconstitution may have caused them to change to kaolinite. Growth of the kaolinite in place is indicated by the large and well-formed crystals within the pebbles. Petrographic evidence indicates that the crandallite in the quarries was formed from allophane.

At one time conglomerate which contained wad probably overlay site 4 (fig. 1). The barium necessary to form the barite at this site may have been derived from this wad, which commonly has a high concentration of barium. Spectrographic analyses indicate that the wad of the quarries still contains considerable barium (about 0.1 percent). Iron sulfides, which are found in the Mansfield Formation (Callaghan, 1948, p. 12), may have been the source of both the sulfate of the barite and the iron of the iron oxide layer that lies between the barite layers.

Not enough critical evidence exists at this small, isolated occurrence for postulation of an origin of the hydrated halloysite, allophane, gibbsite, or wad.

REFERENCES

CALLAGHAN, EUGENE, 1948, Endellite deposits in Gardner Mine Ridge, Lawrence County, Indiana: Indiana Div. Geology Bull. 1, 47 p.

ERD, R. C., 1954, The mineralogy of Indiana (unpublished A. M. thesis): Indiana Univ. 170 p.

LOGAN, W. N., 1922, Economic geology of Indiana, *in* Handbook of Indiana geology: Indiana Dept. Conserv. Publ. 21, p. 662–756.

MALOTT, C. A., 1951, Variations in the stratigraphic position and character of the base of the Mansfield sandstone in southern Indiana: Indiana Acad. Sci. Proc., v. 60, p. 239–246.

PALACHE, C., BERMAN, H., AND FRONDEL, C., 1951, The system of mineralogy of James Dwight Dana and Edward Salisbury Dana. v. 2, 7th ed., 1124 p., New York, John Wiley and Sons, Inc.

ROSS, C. S., AND KERR, P. S., 1934, Halloysite and allophane: U. S. Geol. Survey Prof. Paper 185, p. 135–148.

JOURNAL OF SEDIMENTARY PETROLOGY, VOL. 30, NO. 4, PP. 582–584
DECEMBER, 1960

ACIDITY-ALKALINITY OF SURFACE DRAINAGE WATERS AS RELATED TO UNDERLYING SILICATE ROCKS[1]

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ABSTRACT

Surface drainage waters in humid regions underlain by silicate rocks range in pH from about two units above to several units below neutrality. Alkaline waters were observed in regions underlain by pyroclastic rocks and nepheline syenite, whereas acid surface waters were measured where the underlying rocks were gneisses, granites, and certain other igneous rocks. The pH of the surface water is interpreted as being influenced by the hydrolytic (alteration) products of the rocks—the more alkaline water being associated with the silicate rocks most susceptible to hydrolysis.

INTRODUCTION

The waters of rivers, lakes, and springs, (that is, surface drainage waters) in humid regions of the earth underlain by silicate rocks range widely in pH values. Although such surface waters have commonly been documented as being acid, actually water that is definitely alkaline is found to be abundant, especially in regions where the country rock is composed of pyroclastics. An alkaline condition in rain (and snow) derived water, which is normally acidified by CO_2 dissolved from the air, indicates another stage, following precipitation, of chemical reaction or dissolution of an alkaline substance. It is interpreted that alkalinity was contributed to the waters reported on herein dominantly by the hydrolysis of the silicate rocks with which the waters were in contact.

The pH measurements of the waters were made using a portable glass-electrode meter (Beckman) during July and August, 1959, while collecting rock specimens for an extended study on weathering.[2] Some of the water samples were measured directly in the open-surface, field occurrences of the water, but most of them were collected in pint-size polyethylene bottles and measured in camp at night following the day of collection. As a further check on the instrumental results, fourteen of the samples were shipped to the campus laboratory (University of Missouri) and measurements made in early September with a regular laboratory meter. Deviation between the readings of the two pH meters was never greater than 0.3 pH unit, but readings on the laboratory meter are reported when available.

Conductivity measurements were made at night in camp using a model RC-16B (Industrial Instruments Company) conductivity bridge. The cell was calibrated with a standard conductivity solution but the waters were measured at ambient temperatures without further correction, thus the conductivity data are comparable in order of magnitude but not to small differences.

MEASUREMENTS, OBSERVATIONS, AND DISCUSSION

Data are offered from 16 water samples collected from various igneous and metamorphic localities distributed across the United States and Canada (one sample). The particular spot for collection was chosen so that the water was representative of drainage from the rock or feature with which the water is described. The listing is in order of decreasing pH.

1. Old Faithful Geyser water; pH, 9.2; specific conductance, 950 micromhos, relatively high; country rock is volcanic.

2. Water taken about 3 hours after a summer shower from an intermittent seep in jointed, bare nepheline syenite on "Buttermilk Hill" (housing area of the Aluminum Company of America), Bauxite, Arkansas; pH, 7.9; conductivity not run; country rock is nepheline syenite.

[1] Manuscript received November 30, 1959.
[2] National Science Foundation Grant G-9159, the aid of which in collecting these water samples is gratefully acknowledged. A replicate water sample was kindly furnished by the Park Naturalist, Lassen National Park.

3. Manzanita Lake, Lassen National Park; pH, 7.8; specific conductance, 116 micromhos; country rock is ash and other pyroclastics of intermediate to mafic composition.

4. Jackson Lake, Wyoming; water collected at boat dock at Leek's Lodge; pH 7.7 to 7.8; specific conductance, 96 micromhos; lake impounded by glacial drift, Yellowstone volcanics, and crystalline silicate rocks.

5. Rio Grande River headwaters, South Fork, Colorado, in the eastern San Juan Mountains; pH 7.6; specific conductance, 65 micromhos; country rock is ash and lava of San Juan volcanic group ranging in composition from rhyolite to basaltic andesite.

6. Blackwood Creek, one-fourth mile north of Tahoe Pines, California, on west side of Lake Tahoe; pH, 7.5; specific conductance, 56 micromhos; country rock is composed of pyroclastics of intermediate composition, and granite.

7. West-flowing creek near top of west side of Twogwotee Pass, Absaroka Mountains, Wyoming; pH, 7.5; specific conductance, 55 micromhos; country rock is ash and coarser pyroclastics of intermediate to mafic composition.

8. Yellowstone Lake, water collected near West Thumb Village, Wyoming; pH, 7.35; specific conductance, 78 micromhos; country rock is mainly rhyolitic lava and ash.

The foregoing eight samples (half of the set) are above 7 in pH and are therefore classified as "alkaline" in deference to the reference pH of pure water. A more significant reference pH with respect to rain water and the subsequent modification (rise in pH) of it would be the pH of falling rain (actually a range of values, 5.5 to 6.5). Any pH significantly above or below this range in drainage water signifies some sort of reaction or dissolution. Alkaline waters (above pH 7) mean simply a higher degree, but of the same kind, of modification as that undergone by a drainage water having pH 6.9, for example.

Nevertheless, it is observable that the alkaline waters cited in the preceding list drained silicate rocks which contained large ratios of ash, a glassy phase in volcanic rocks or, in one instance, nepheline. A silicate glass is notably susceptible to hydrolysis, as is well known from its reaction with water in laboratory glass utensils, as well as from geologic field observations. The fine particles of glass in vitric ash present a relatively large surface area to water and they, with the high permeability and porosity of ash deposits, conduce toward optimum conditions for hydrolysis. Hydrolysis of ordinary silicate rocks develops an alkaline solution, as has long been known (Stevens, 1934; Keller, 1957). Nepheline syenite, such as in the Arkansas occurrence, exhibits a high abrasion pH (Stevens and Carron, 1948; Keller, 1958) that is compatible with easy hydrolysis, and yields an alkaline solution. Thus, the alkalinity of the water draining from the rocks is interpreted as arising primarily from the alteration of the rocks and, significantly, from the kinds of rocks that develop high alkalinity upon hydrolysis.

Additional water samples ranging in pH from 7 to 2.9 are reported below. Probably the hydrolysis of mafic rock, as in sample No. 9, and its drainage water at pH 7, are more closely related to representatives above pH 7 than below it, but the break in the list has been made at chemical neutrality.

9. Lake Superior, at Flood Harbor, about 15 miles north of Duluth, Minnesota; pH, 7.0; specific conductance, 115 micromhos; local country rock is mafic.

10. Seep water, Auburn Iron Mine, near Eveleth, Minnesota; pH, 6.9; specific conductance, 115 micromhos; country rock is Precambrian iron formation.

11. Popo Agie (Middle Fork) River, Sinks Canyon, Lander, Wyoming; pH 6.85; specific conductance, 30 micromhos; country rock is granodiorite and granite gneiss.

12. Dinwoody (glacial) River, Wind River Mountains, near Dubois, Wyoming; pH, 6.8; specific conductance, 21 micromhos; country rock is mainly granite gneiss.

13. Sylvan Lake, Black Hills, South Dakota; water from northeast side of lake; pH, 6.7; specific conductance, 89 micromhos; country rock is granite and schist.

14. Lake Nipissing, at North Bay, Ontario; pH, 6.6; specific conductance, 97 micromhos; glacial drift rich in gneiss and schist.

15. Spring issuing from gneiss on U. S.

211, about 1 mile west of east entrance of Shenandoah National Park, Virginia; pH, 6.4 to 6.5; specific conductance, 37 micromhos; country rock is gray gneiss and schist.

16. Hot spring at the "Sulphur Works," Lassen National Park; pH, 2.9; specific conductance, 1800 micromhos; relatively high acidity due to sulphur compounds in ascending hot water. Note the contrast in acidity of this "sulphur water" with the alkaline water of Old Faithful Geyser, No. 1.

The silicate rocks whose drainage waters (cited above) yield pH values below 7 are typically granitic rocks and corresponding gneisses and schists. The pH of these waters has been modified but little from that of their rain water source for probably the following reasons (apart from theoretically short-time contact with the rocks): (1) relatively slow hydrolysis because of the coarse texture (low specific surface area) of the mineral particles in granitic rocks, (2) lower reactivity of the relatively high silica minerals, and (3) the characteristically low abrasion pH (Stevens and Carron, 1948) of the constituent rocks and minerals.

The chief purposes of this report are to direct attention to the abundance of surface drainage waters which are higher in pH than is fresh rain water, and that lakes and streams of large size may be alkaline in reaction. Geologic implications of particular pH values, and likewise of changes of pH across certain critical values, may be exceedingly important both to sedimentary rocks and to mineral deposits. For example, the abstraction or deposition of silica and carbonate minerals in sedimentary rocks, mineral replacements and deposition including valuable deposits of ore minerals in sedimentary rocks, and increase or decrease in porosity in the rocks may be governed by the pH of the transient solutions. That drainage waters may be alkaline, as well as acid (which has been more widely documented) should come into the consideration of sedimentary petrologists and general geologists.

REFERENCES

KELLER, W. D., 1957, Principles of Chemical Weathering. Lucas Bros., Columbia, Mo., 111 p.

———, 1958, Argillation and direct bauxitization in terms of concentrations of hydrogen and metal cations at surface of hydrolyzing silicates: Am. Assoc. Petroleum Geologists Bull., v. 42, p. 233–245.

STEVENS, R. E., 1934, Studies on the alkalinity of some silicate minerals: U. S. Geol. Survey Prof. Paper 185, 13 p.

STEVENS, R. E., AND CARRON, M. K., 1948, Simple field test for distinguishing minerals by abrasion pH: Am. Mineralogist, v. 33, p. 31–50.

JOURNAL OF SEDIMENTARY PETROLOGY, VOL. 30, NO. 4, PP. 585–588
FIGS. 1–2, DECEMBER, 1960

CHAMOSITE OOLITES IN THE DEVONIAN OF PENNSYLVANIA[1]

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The Johns Hopkins University, Baltimore, Maryland

ABSTRACT

Previously described "spore-like fossils" in a black silty shale in the Devonian Montebello Sandstone, north of Harrisburg, Pennsylvania, were restudied and found to be flattened chamosite oolites. The environment in which the oolites formed was marine, slightly reducing, having a small clastic influx, and with currents strong enough to agitate sand grains.

Cramer (1958) described spore-like fossils (*Tasmanites rockvillensis* n. sp.) in a black shaly siltstone in the Devonian Montebello Sandstone at the northernmost Rockville quarry, 2½ miles north of Harrisburg, Pennsylvania. These "spores," restudied by the authors, proved to be flattened chamosite oolites.

Willard (1939) described the stratigraphy and paleontology of the Rockville quarries. The oolites occur in a black, fossiliferous shale at the base of 55 ft of dark gray, thin-bedded, fossiliferous silty and sandy shale (Willard's unit 4). A light gray, thick-bedded, coarse-grained, fairly well-sorted quartzose sandstone occurs beneath the oolitic unit. Marine fossils occur in the sandstone although they are not common.

The oolite-bearing black silty shale is 3 ft thick and contains abundant marine fossils. Oolites are mostly confined to small lenses parallel to bedding. Scattered small rounded pebbles and sand grains of quartz occur in the basal part of the black shale and in the oolitic lenses. Both oolites and quartz grains decrease in abundance toward the top of the unit. Subspherical collophane nodules up to 25 mm in diameter are randomly distributed throughout the oolitic unit.

The oolite-bearing shale is also exposed at the north end of the roadcut in Little Mountain along U. S. Route 11 where it has the same stratigraphic position as in the Rockville quarry. The shale is badly weathered and coated with brown iron oxide. Even the oolites are strongly oxidized. Lesley (1892) described a thin bed of "fossil ore" from the northern slope of Little Mountain and various other localities in Perry County, Pennsylvania. Although Lesley mentioned neither chamosite oolites nor specific iron minerals, it seems likely that he was dealing with the oxidized chamositic unit. Oxidized oolitic chamosite also occurs at the top of the Montebello Sandstone in Dauphine County, 3 miles north of Amity Hall on U. S. Route 322.

The oolites are black, shiny, disc-shaped, and range from 1 to 2 mm in diameter. Generally, they are oriented parallel to bedding. A few display distinct concentric markings; many possess a raised central area which can be identified with the hand lens as a rounded quartz nucleus. Their thickness is a small fraction of their width. However, the oolites included in collophane nodules and those protected by shell fragments are only slightly flattened.

In thin section chamosite oolites and other sand-sized grains are seen to be scattered through a fine-grained matrix (fig. 1). The oolites and other larger grains, which make up less than one-third of the rock, tend to be concentrated in lenses. They are recognized as oolites by their nuclei and concentric structure and by their spherical form where protected from flattening after deposition. Broken oolites serving as nuclei for further oolitic growth show that the oolites formed before final deposition of the sediment.

The oolites are composed principally of a mineral occurring as minute flakes disposed tangentially to the spherical structure. This mineral grades from a pale green variety marked by slight pleochroism and first order gray interference colors to a

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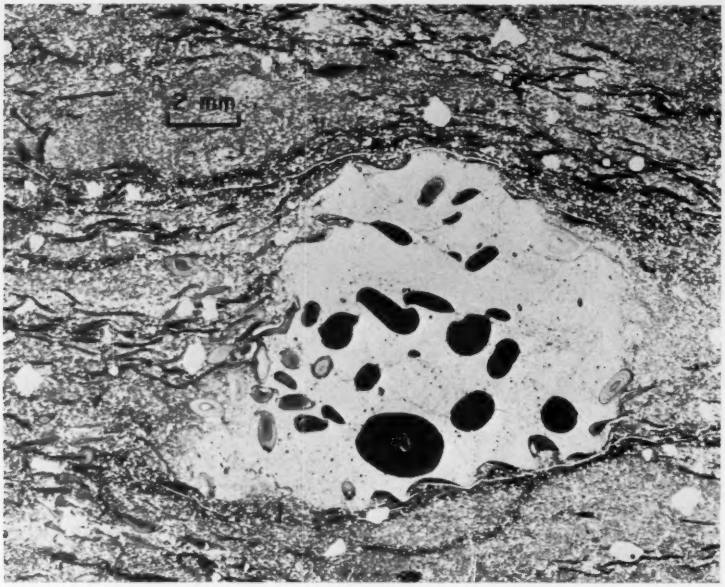

FIG. 1.—Oolite-bearing silty shale with collophane nodule. Note that the oolites within the nodule are less flattened than those outside the nodule. Section is perpendicular to bedding. Ordinary light.

brown variety which has stronger pleochroism and first order yellow interference colors. The change in color from green to brown probably results from slight oxidation. Powder patterns of the oolites taken with a Phillips X-ray diffractometer were not definitive but showed strong peaks at 7Å and 3.5Å which indicate either a 7Å chlorite or an iron-rich 14Å chlorite (Brindley, 1951; Brindley and Gillery, 1956). This mineral may be called chamosite in the broad sense of the term.

Some oolites have concentric shells of collophane and several are composed entirely of this substance. One broken collophane oolite is surrounded by a shell of chamosite, so the collophane must be a product of direct precipitation or at least sea floor replacement of chamosite. X-ray powder patterns show that the collophane has an apatite crystal structure.

Nuclei of the oolites are most commonly quartz sand grains (fig. 2). Other nuclei include quartzite grains, carbonate grains, chlorite flakes, a collophane flake, a chert grain, a basic volcanic rock fragment containing small feldspar laths, and several fragments of broken oolites. Some oolites have no apparent nuclei. The wide variety of nuclei should remove any doubts that these bodies are oolites rather than spores.

The most notable feature of the chamosite oolites is their extreme deformation. They are flattened parallel to bedding and generally their long dimensions are 15 times greater than their short dimensions. Quartz sand nuclei commonly push through the concentric shells. In contrast, the oolites within collophane nodules exhibit only minor deformation.

These collophane nodules contain scattered oolites, quartz grains, and other detritus similar to that in the matrix. The nodules have somewhat gradational boundaries, and oolites extend across these boundaries, suggesting that the nodules formed by diagenetic segregation of collophane and partial replacement of the matrix material previously present. They evidently formed early during diagenesis

FIG. 2.—Flattened chamosite oolite with quartz nucleus. Ordinary light.

and were competent enough to protect the enclosed soft chamosite oolites from compaction. Chamosite oolites within the nodules have been partially replaced by carbonate.

The chamosite oolites are associated with other sand grains, such as detrital quartz and quartzite, brachiopod and crinoid fragments, and rare collophane flakes which are probably fragments of lingulid brachiopods. The quartz sand averages .5–.7 mm in diameter and has an estimated roundness of .5–.6.

The matrix consists predominantly of sericite, angular quartz silt and very fine sand, pale green chlorite, and pale brown collophane. The chlorite resembles the pale green variety in the oolites and probably is also iron-rich. Some of the chlorite occurs as granules averaging approximately 0.1 mm in diameter. The chlorite in these small granules is unoriented. Less common constituents of the matrix are pyrite, carbonate (both calcite and siderite were identified by X-ray powder patterns), carbonaceous matter, leucoxene, and detrital muscovite, biotite, and feldspar. The sericite and other platy grains of the matrix tend to lie parallel to the bedding, producing a normal shaly fissility. Several paragenetic relationships of limited extent are evident: chlorite replaces detrital quartz, feldspar, biotite, and calcite fossil fragments; carbonate (siderite?) replaces quartz grains, chamosite oolites, and fossil fragments; and pyrite replaces fossil fragments and chamosite oolites.

The association of oolites and other large detrital grains with a fine-grained matrix is unusual. The authors do not interpret this as simultaneous deposition or the growth of oolites in place. Probably the matrix formed by slow clastic and chemical sedimentation in quiet water and the oolites and associated larger grains were deposited by fluctuating currents. Evidently the sand influx and rate of oolite growth were so slow that there was seldom a sufficient supply of oolites and sand to cover the depositional surface completely.

As has been stated, collophane and an

iron-rich chlorite occur both in the matrix and in the oolites. This mineralogical similarity strongly suggests that the oolites formed essentially where they are now found, having undergone only slight transportation. Chemical sedimentation must have occurred during times of mud deposition in quiet water as well as during times when currents were strong enough to agitate sand grains. The currents were presumably not active enough to oxygenate the water completely, for otherwise hematite oolites would be expected to form. The environment in which the oolites formed can be summarized as marine, slightly reducing, having a small clastic influx, and with currents strong enough to agitate sand grains. An analysis of the chemical conditions necessary for the deposition of this unusual rock is beyond the scope of this paper.

Inasmuch as the "spores" previously described by Cramer are not organic, the authors wish to caution other workers in their identification of small, dark, flattened or spherical objects occurring in black shales, especially the Devonian shales of the Appalachian region. Chamosite oolites probably have been overlooked in the past and a restudy in thin section of problematic spores may reveal their true nature.

Another line of evidence suggesting that chamosite is more common in the Devonian than previously realized is the reported occurrence of ferruginous oolites in the Needmore Shale of Virginia (Lesure, 1955), Boyle Limestone of Kentucky (Bucher, 1918), and Tully Limestone of New York (Cooper and Williams, 1935). None of these authors specifically state that the oolites are chamositic. Their descriptions, however, suggest to the present authors that the oolites are composed of chamosite. Probably a critical reexamination would establish their mineralogical identity.

ACKNOWLEDGMENT

The authors are very grateful to Dr. F. J. Pettijohn for his constructive criticism and suggestions during the preparation of this paper.

REFERENCES

BRINDLEY, G. W., 1951, The crystal structure of some chamosite minerals: Mineralog. Mag., v. 29, p. 502–525.

BRINDLEY, S. W., AND GILLERY, F. H., 1956, X-ray identification of chlorite species: Am. Mineralogist, v. 41, p. 169–186.

BUCHER, W. H., 1918, On oolites and spherulites: Jour. Geology, v. 26, p. 593–609.

COOPER, G. A., AND WILLIAMS, J. S., 1935, Tully Formation of New York: Geol. Soc. America Bull., v. 46, p. 781–868.

CRAMER, H. R., 1958, Additions to the Hamilton biota at Rockville, Dauphin County, Pennsylvania: Pennsylvania Acad. Sci. Proc., v. 32, p. 186–187.

LESLEY, J. P., 1892, A summary description of the geology of Pennsylvania: Pennsylvania Geol. Survey, 2nd ser., Final Rept., v. 2, p. 721–1628.

LESURE, F. G., 1955, Geology of the Clifton Forge iron district, Virginia: Unpublished Ph.D. dissertation, Yale University, 186 p.

WILLARD, B., 1939, The Devonian of Pennsylvania: Pennsylvania Geol. Survey, 4th ser., Bull. G-19, 841 p.

JOURNAL OF SEDIMENTARY PETROLOGY, VOL. 30, NO. 4, PP. 589–602
FIGS. 1–22, DECEMBER, 1960

SOME FEATURES OF MODERN BEACH SEDIMENTS[1]

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ABSTRACT

Studies of selected tidal flats on the Maine coast give opportunity to observe a variety of sedimentary features in the making. Varieties of ripple mark, rill mark, grain size distribution, beach chutes with "flow" marks, mounds, mud pebbles, and primary lineation are figured and briefly discussed.

INTRODUCTION

Fluctuations in clam (*Mya arenaria*) production have caused the Maine Department of Sea and Shore Fisheries to select certain intertidal areas for detailed investigation. The areas selected vary in type of sediment, configuration, and biological assemblages. A series of repeated mappings on large scales is projected to discover if significant measurable changes are taking place. Dr. W. H. Bradley, of the U. S. Geological Survey, has been engaged in similar studies of an intertidal zone at Georgetown, Maine.

It is commonly recognized that geologists engaged in studies of ancient sediments or metasediments might profitably spend some time in the study of present day sedimentary processes on modern beaches. The authors are familiar with some of the many excellent and beautifully illustrated articles dealing with similar subjects but hope that a few notes and illustrations of present day sediments and features so keenly observed by such workers as Twenhofel (1932), Bucher (1919), Kindle (1917) and Pettijohn (1957) may be worthwhile. This paper illustrates and comments briefly on a few of the features of the intertidal zone: ripple mark and related minor structures, rill and frost mark, lineation, mud balls, mounds, and preservation or burial.

RIPPLE MARK

The portion of the Maine coast known as Western Beach at Scarborough offers an excellent opportunity for the study of ripple mark because it contains many acres of rippled intertidal flats. A portion of the rippled area is shown in figure 1. The ripples are current ripples with recognizable asymmetry, constructed largely by the incoming tides and modified by the outgoing tides. The steeper face of the ripple is in general the shoreward side, and in general the ripple axis parallels the shoreline. Ripple indices of four to six are common.

Bifurcation of ripples.—In addition to ripple index, another ratio might be mentioned which appears to be a function of homogeneity of surface (both slope and material). This is the bifurcation of individual ripple crests per unit crest length. This may vary also with the fetch and frequency of the waves. Figure 2 illustrates this bifurcation. Apparently fewer bifurcations per unit distance are found in the deeper water parts of the beach. Possibly this is because the slopes and materials tend to be more uniform on the outer parts of Western Beach where they were noted. At the time Western Beach was studied, many of the ripples bifurcated two or three times in a hundred feet; some individual ripple crests, however, extended undivided for well over a hundred feet. Data for statistical analysis were not collected.

Grain size distribution.—The distribution of the larger grains in the troughs of the current ripples is very evident (fig. 3). This is a feature of current ripple that may be of help in studying deformed sediments that have preserved ripple mark, because it aids in distinguishing tops of beds from bottoms. In figure 3 the ripples have been somewhat bevelled. When preserved, these ripples give the appearance of being inverted. The

[1] Manuscript received February 5, 1960.

FIG. 1.—Portion of Western Beach, Scarborough, Maine.

FIG. 2.—Bifurcation of ripples.

coarse grain in the troughs is diagnostic, however. In figure 4 winrows of shells and coarser fragments lie in the troughs. Shells, so concentrated far beyond their living densities, may be buried by bevelling the ripples. In the photo many of the *Mya* have both valves intact and together. This figure may help to explain certain distributions of fossils.

Superposed ripples.—Another phenomenon that appears frequently on Western Beach and other similar rippled flats is superposed ripple mark. The superposed ripples may parallel the crests of the earlier ripples or cross them at a high angle. Figure 5 shows superposed ripples of the parallel type. The larger ripples were formed earlier, probably at high tide because of the greater wave length and amplitude. As the tide ebbed or wind and wave diminished, waves of shorter length notched the crests but did not fetch into the troughs of the earlier ripples. This feature is also a criterion for determination of tops and bottoms when preserved in sedimentary rocks. The authors suggest that in the lower parts of the beach long wave length ripples, which formed when the tide was high and the winds strong, may persist through two or more successive tide cycles. That this is true in offshore zones has been demonstrated by observations of ripple persistence through vertical sections of several feet. The point may have some significance, for if ripples in the tidal zone are completely destroyed and rebuilt in each tidal cycle, a minimum thickness of the tidal churning or reworking of the beach is afforded by the ripples. If, on the other hand, ripples are gradually modified and destroyed through a more or less extended period, a somewhat different ecological picture is presented (Note figure 21).

Superposed ripples at a high angle to the earlier ripples are shown in figure 6. This relationship may have been misidentified as an interference result in some studies of consolidated sediments. On Western Beach flood tide currents are generally stronger than ebb tide currents. To the south this beach faces open sea, and also faces an estuary to the west in the area studied. The tides rise over the flat and ebb somewhat less rapidly with drainage from the western part of the beach occasionally towards the

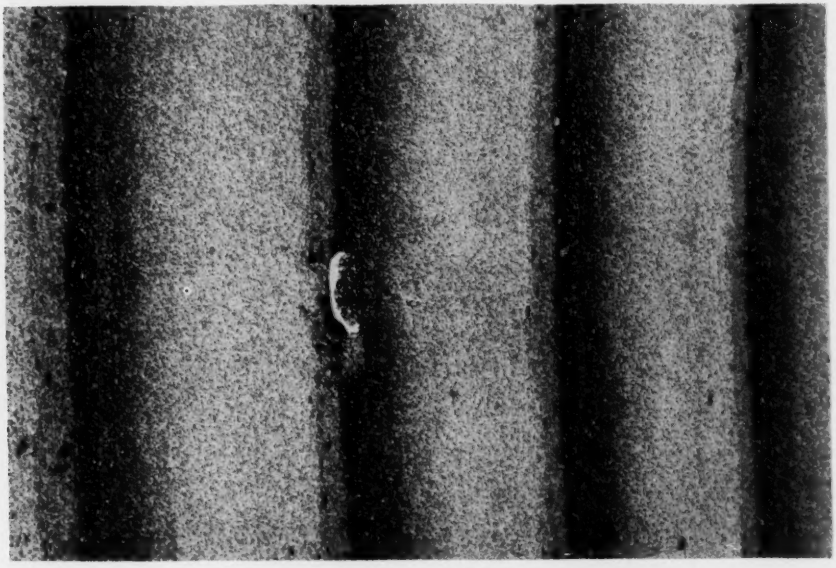

FIG. 3.—Ripples with coarser sand in troughs than on crests.

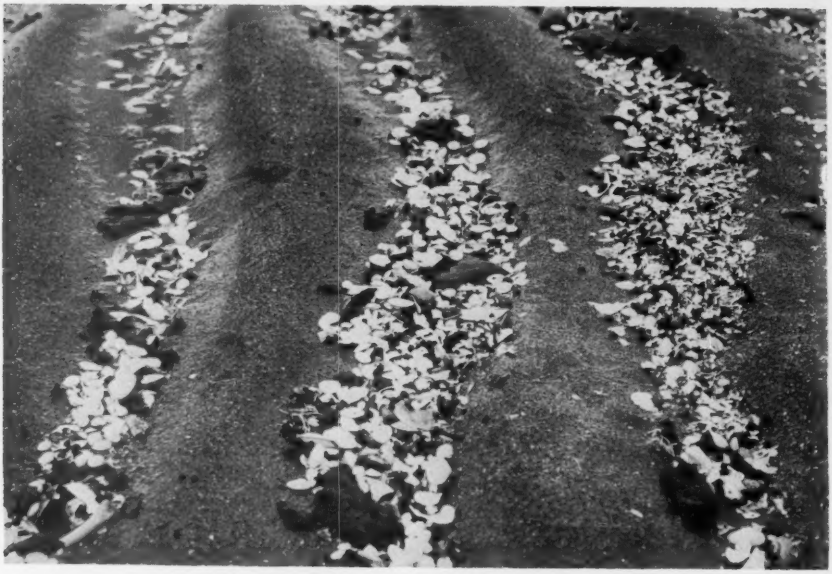

FIG. 4.—Shell windrows in ripple troughs.

FIG. 5.—Superposed ripples, Western Beach, Scarborough, Maine.

FIG. 6.—Superposed ripples, Scarborough, Maine.

estuary. This drainage with the rippling at high angle to the major ripples is shown in the submerged portion of the foreground of figure 7. The resulting sand ripples are shown in figure 8. Cross ripples are not formed on every tide, however, and the ordinary tide drains off the flat to the south. The lateral drainage evidently is aided by a cross-wind.

That the flood tide currents are generally stronger than those of the ebb tide is shown by the infrequent reversal of asymmetry of the major ripples so that the gentle or back slope of the ripple faces the shore. The general lack of reversal of the scour and mounding about objects on the tidal flats, waterlogged logs, stakes, or boulders also indicates that the flood tide currents are in general, more effective, than those of the ebb tide.

Overhanging Ripples and Beach Chutes.—The authors were somewhat surprised to find overhanging ripples as shown in figure 9. The explanation of these overhanging ripples is apparent from figure 10. The ripple troughs are frequently the drainage lines for the last few inches of ebb tide drainage. The authors have not seen this feature in consolidated sediments, but if they could be filled and preserved, with incomplete exposures, the structure might be interpreted as small scale asymmetric folding or flow features of soft rock deformation. Grain size distribution or primary lineation might give a clue to origin. It is difficult to picture conditions for preservation of this structure; wind deposit might bury them locally.

Related to the lateral drainage along ripple troughs are channels we have called "beach chutes." (figs. 11 and 12). One of the streams along the trough of a ripple breaks across the ripple and forms a stream at a high angle to the ripple. As tributaries are picked up, velocities are such that sand, pebbles, or shells are carried along and deposited in the low water zone or left along the chute. In homogeneous rather fine sand flow marks, which resemble "load casts," are left as shown in fig. 12

RILL MARK

Rill mark is very common on the beaches examined. As the tide level drops, the water table also drops, but generally a little more

FIG. 7.—Lateral drainage off Western Beach. Foreground is submerged. Note rippled water in troughs.

FIG. 8.—Superposed ripples.

FIG. 9.—Overhanging ripples, Scarborough, Maine.

FIG. 10.—Origin of overhanging ripples by lateral drainage.

FIG. 11.—Beach chute (named after similarity to an old-fashioned coal chute).

FIG. 12.—Beach chute in homogeneous sand (note "flow marks" in bottom of chute).

slowly than the tide. This depends, of course, on the permeability of the beach material. The interstitial water drains down the beach and forms surface rills. Contact or water table springs develop where an underlying difference in permeability or intersection of the beach surface and its water table bring the water out onto the beach. These rills generally bifurcate seaward. Rill mark is shown in figure 13.

The network of drainage in the finer materials appears to be the origin of frost mark as shown in figure 14. This picture was taken near the top of a beach on a frosty morning. It is possible that this type of mark, preserved, has been identified as organic in origin.

LINEATION

Primary lineation is frequently developed on the surfaces of sand and silt beaches. It forms on both rippled and non-rippled surfaces. The structure is so common that it appears to the writers that most shallow water silt and sand deposits display this characteristic. Lineation can be seen in the making at the water's edge. Streaks of micas are very common, and streaking is also evident in other mineral and rock particles. This is a lineation in the transport direction, or in the nomenclature of tectonites, lineation in *a*. Possibly some of the mica streak type of lineation seen in some gneisses and schists may be in part a mimetic structure of this origin. Figure 15 shows this type of lineation faintly. At other locations the streaking was both more pronounced and more widely spaced.

Another type of lineation that can be seen in process of making also is shown in figure 16. The lineation here is a ridge and furrow type, localized by the distribution of coarser pebbles in the sand. The back and forth swashing of the waves causes the lineation. A somewhat similar lineation, (fig. 17) seems to have been caused by the back and forth wave swash of a cross rippled area of the type shown in figure 7 or 8.

MUD BALLS

At Maquoit Bay a silty clay tidal flat is backed by a sea cliff cut in the silty clay of

FIG. 13.—Rill mark.

FIG. 14.—Frost mark.

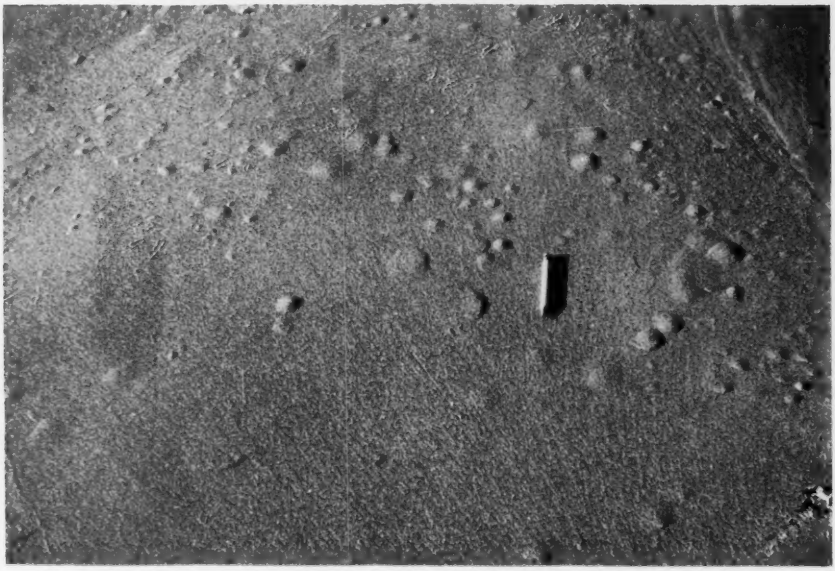

FIG. 15.—Mounds and fine lineation due to mineral streaking slanting down to right. (Pencil approximately 4 in. long).

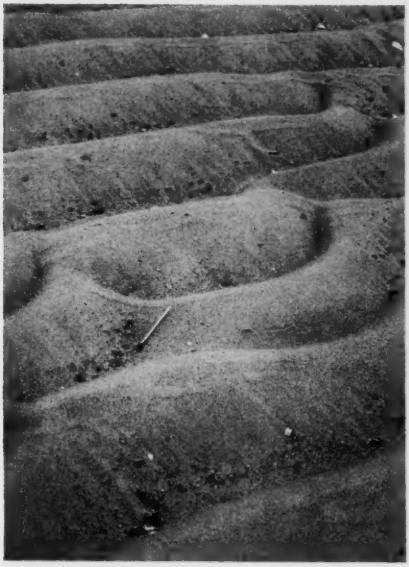

FIG. 16.—Lineation on ripple mark, ridge and furrow type.

FIG. 17.—Lineation on ripple mark.

FIG. 18.—Sea cliff in silt, source of clay pebbles Maquoit Bay, Maine.

FIG. 19.—Clay pebbles, Maquoit Bay, Maine.

FIG. 20.—Sand mass encroaching on rippled area.

glacial origin. This deposit is cracked and jointed and furnishes at times blocks of silty clay that are rolled around by exceptionally high tides. The situation is shown in figure 18. The clay pebbles, many of which at the time of our observation were about the size of potatoes, had become so indurated that a hammer blow was necessary to break them. A group of these pebbles is shown in figure 19. The crab (*Limulus*) has a crosswise measurement of approximately 4 in. The pebbles were spread quite widely over the upper part of the beach. A month later when the beach was revisited all the clay pebbles had disappeared, [apparently having lost their identity by being softened and spread on the beach]. This seems to be one way intraformational conglomerates can be formed. The writers have seen lithologically similar intraformational conglomerates in Silurian (?) beds in the vicinity of North Anson and elsewhere in that part of Maine in strongly deformed position.

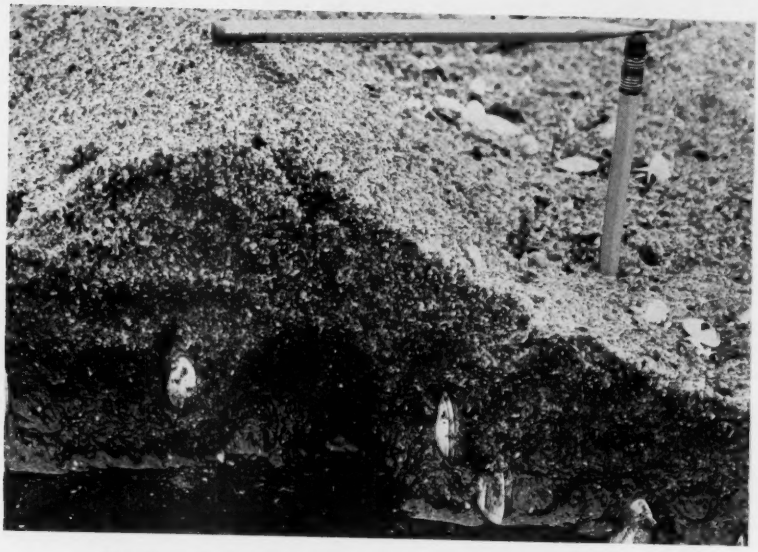

FIG. 21.—*Mya* in ripple. Individuals approximately 5–7 years old.

FIG. 22.—Detail of burial of ripples.

MOUNDS

Small mounds were observed to form in front of the advancing tide (fig. 15). It seems that the air is forced out of the sand with the rise of tide thus building up the sand into these minature mounds. This is a type of structure that might be considered in consolidated sediments to be rain prints, with beds inverted.

PRESERVATION

The preservation of more or less delicate and certainly generally ephemeral surface structures is frequently a surprise to many people, and the authors were fortunate to see in some detail processes of possible preservation. Figure 20 shows the advance of a body of sand over the rippled surface of the flat. In this particular area, the sand is smothering out *Mya*, shells of which are shown in growth position in the rippled beach (Fig. 21). The advance of this "sand front" was followed in some detail in the course of mapping the beach. The burial of ripples is shown on a more detailed scale in figure 22. Although surface features such as ripples possibly are buried, exhumed, destroyed, and rebuilt over and over before passing into the stratigraphic record, it is interesting to note a burial that might preserve the structures.

The authors have presented little that may be new in these notes and photos but think that there may be merit in emphasis by repetition especially since the present holds the key to the past so surely and so obviously in the interpretation of sedimentary rocks.

REFERENCES

BUCHER, W. H., 1919, On ripples and related surface forms and their peleogeographic interpretation: Am. Jour. Sci. ser 4, v. 47, p. 149–210.

KINDLE, E. M., 1917, Recent and fossil ripple mark: Geol. Survey Canada Mus. Bull. 25, 56 p.

PETTIJOHN, F. J., 1957, Sedimentary rocks. 2nd ed., Harper and Brothers, New York, 718 p.

TWENHOFEL, W. H., 1932, Treatise on sedimentation. 2nd ed. Williams and Wilkins Co., Baltimore, 926 p.

JOURNAL OF SEDIMENTARY PETROLOGY, VOL. 30, NO. 4, PP. 603–612
FIGS. 1–4, DECEMBER, 1960

TECHNIQUES IN SEDIMENTARY GEOCHEMISTRY: (2) DETERMINATION OF THE FERROUS IRON CONTENTS OF CARBONACEOUS SHALES[1]

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ABSTRACT

A method is described for the determination of ferrous iron contents in shales containing organic matter up to 4 per cent carbon equivalent. After initial attack on the shale the ferrous iron is made to react with iodine monochloride and the liberated iodine titrated against standard potassium iodate. The value of ferrous iron determinations in shales is illustrated by consideration of the composition of various members of a British Coal Measure cyclothem.

INTRODUCTION

In an earlier paper (Hirst and Nicholls, 1958) a method of determining the non-detrital trace element contents of sedimentary rocks was suggested. In order to make full use of the data acquired by the use of this method it is desirable to know the physicochemical conditions (for example, pH, Eh) under which the sediment accumulated. The work of Garrels and his associates (Castaño and Garrels, 1950; Krumbein and Garrels, 1952; Huber and Garrels, 1953; Huber, 1958) has shown that the possible range of these conditions may be deduced from the nature of various iron-bearing minerals present in the rock. When, in fine-grained rocks (for example, shales, mudstones), the content of the diagnostic minerals is too small for their certain detection by optical or X-ray methods, useful information may be obtained from the chemical composition of the rocks. Where feasible the distribution of iron between the ferric and ferrous condition should be determined, but the presence of organic matter (of frequent occurrence in unmetamorphosed shales and mudstones) complicates this determination. It has long been realized that when organic matter is present in the analysed material unreliable results will be obtained for FeO contents if determined by the usual permanganate method (Washington, 1930, p. 211). Groves (1951, p. 88) observes that "FeO determinations on such rocks can at best be regarded as approximate." Hillebrand, Lundell, Bright and Hoffman (1953) consider that the presence of organic matter in rocks makes the determination of ferrous iron contents "altogether unreliable" (p. 917) or even "impossible" (p. 916). It is not surprising, therefore, that the determination of the FeO contents of carbonaceous shales and other fine-grained rocks is often not attempted. This paper presents details of a rapid method of FeO determination which gives acceptable results in the presence of organic matter up to 4 percent carbon equivalent. It has been used in the analysis of mudstones and shales from the British Carboniferous; in almost all the samples so far studied the organic content is well below this upper limit.

ANALYTICAL PROCEDURE

The method adopted for the determination of the FeO contents of carbonaceous shales is based on the Andrews-Jamieson procedure which was applied to the determination of iron more than thirty years ago by Heisig (1928). In this procedure ferrous-iron bearing solutions are permitted to react with iodine monochloride solution in the presence of a large excess of hydrochloric acid, the liberated iodine being titrated against standard potassium iodate solution using carbon tetrachloride as indicator. Heisig discussed the reactions involved in the titration (see also Belcher and Wilson, 1956, p. 172–173) and demonstrated that various organic compounds do not interfere with the titration. Smith and Wilcox (1942) suggested the use of certain dyestuffs as

[1] Received January 21, 1960.

internal indicators, particularly Amaranth (British Colour Index Number 184), and confirmed that the method is satisfactory in the presence of a number of organic compounds. Hey (1949) has applied this method of titration to the determination of FeO in silicates after initial attack with a mixture by hydrochloric and hydrofluoric acids in the cold. Details of his procedure are given by Groves (1951, p. 93). Attempts to apply the Hey technique to the determination of FeO in Coal Measure shales gave inconsistent results which in some cases were clearly erroneous, as when the determined FeO content exceeded the total iron content of the sample. His method of attack was therefore abandoned in favour of that given below. When organic matter is present it is clearly desirable to break the rock down and complete the titration as rapidly as possible to prevent possible reduction of ferric iron during the determination.

One-half gm of sample was weighed out in a Palau or platinum crucible of approximately 20–25 cc capacity and to this 10 cc 1:1 H_2SO_4 and 5 cc 40 percent HF were added. The crucible was covered with a well-fitting lid and heated over a radiator so that the contents were kept gently simmering for 5 minutes. (This period is adequate for the breakdown of shales—the shorter the period during which complete breakdown can be achieved the better.) When the breakdown was judged to be complete the crucible contents were poured into a 100 cc beaker containing 2 gm of solid boric acid[2] and both the crucible and its lid well washed with cold boiled distilled water, the washings being collected in the beaker. The solution in the beaker occupied approximately 50 cc at this stage.

The solution in the 100 cc beaker was then poured into a stoppered bottle containing 75 cc concentrated HCl and 6 cc iodine monochloride solution (prepared by dissolving 10 gm KI and 6.44 gm KIO_3 in 150 cc 1:1 HCl). The beaker was well washed, the washings passing into the bottle until the volume of solution therein totalled 145–150 cc. Ten cc pure carbon tetrachloride were added and the bottle was stoppered and well shaken for 20 seconds. At this stage the carbon tetrachloride layer below the aqueous solution was a deep mauve (iodine colouration) and heavily charged in its upper part with the carbonaceous matter which tends to collect at the interface between the two immiscible liquids. Standard potassium iodate solution was added from a burette with intermittent shaking of the bottle until the mauve colour had almost disappeared from the carbon tetrachloride layer. An additional 10 cc of carbon tetrachloride were then added to form a zone free from carbonaceous matter at the bottom of the bottle in which the end-point (disappearance of colour in the carbon tetrachloride) could be easily detected. Toward the end of the titration the contents of the bottle were well shaken after the addition of each drop of the potassium iodate solution.

Since total iron contents of the rocks analysed were determined by titration with permanganate after appropriate reduction, the potassium iodate solution was standardised against the permanganate so that correlated results could be obtained. This was easily achieved by preparing a ferrous sulphate solution (approximately 15 gm/litre) and titrating 25 cc aliquots of this solution against both the iodate and permanganate solutions. From the known iron equivalent of the permanganate solution the iron equivalent of the iodate solution was then readily obtained. Where other methods of determining total iron contents are adopted (O'Neil, 1959, p. 272), similar correlation of standards would be required.

It should be noted here that the method of attack used leaves any pyrites in the rock virtually unaffected. The iron content of

[2] If solid boric acid is omitted from the procedure, aberrant results are obtained. Variable blanks are obtained if a hot mixture of sulphuric and hydrofluoric acid is added directly to the iodine monochloride in the titration vessel; it is possible that this is caused by decomposition of the iodine monochloride by hydrofluoric acid. A detailed examination of the cause of the variable blanks, which are not obtained if the excess of hydrofluoric acid is countered by boric acid as suggested, has not been made. It appears likely that the inconsistent results obtained when the Hey method of attack was used are due to the same cause, though it is not clear how boric acid could be used to counter excess hydrofluoric acid in the Hey procedure.

this mineral is, therefore, reported as Fe_2O_3.

ACCURACY AND PRECISION OF THE METHOD

In the absence of reliable sedimentary rock standards, the Centerville diabase (W1), was chosen for accuracy tests. Even this much analysed rock (Fairbairn and others, 1951) is not entirely satisfactory since the spread of determined FeO contents is disconcertingly wide. (Fairbairn, 1953). Using the method of FeO determination given here the following values were obtained:

8.90%, 8,91%, 8.91%.

These are well within the range quoted by Fairbairn, though higher than his arithmetic mean of 35 determinations (8.71%). However, the arithmetic mean of determinations by 6 analysts in the laboratory of the U. S. Geological Survey is 8.91% (Fairbairn and others, 1951, p. 38, table 17) with which the above figures are in satisfactory agreement. The Westerly granite (G1) was analysed twice, the values obtained for FeO being 1.03% and 0.96%. These are both well within the range quoted by Fairbairn (1953) and reasonably close to his arithmetic mean of 35 determinations (0.99%). In the absence of organic matter the method appears, therefore, to give results of comparable accuracy to those obtained using other methods of FeO determination.

Natural organic matter in shales and mudstones is much more complex than the simple organic compounds used in the investigations of Heisig (1928) and Smith and Wilcox (1942). In order to investigate the effect of natural organic matter on the accuracy of this method a synthetic standard was prepared by mixing the diabase W 1 with organic matter, which is probably reasonably close in composition to the carbonaceous matter in shales. Elaterite from Windy Knoll, Derbyshire, England, was used (for details of this material see Mueller, 1954). Using a value of 8.91% for the FeO content of W 1, the synthetic standard contained 4.4% elaterite and, therefore, 8.52% FeO. The determined FeO contents of this standard were 8.56%, 8.54%, 8.54%, that is, they are very slightly higher than the calculated contents. W 1 contains over 1% Fe_2O_3 (Fairbairn and others, 1951) and since it is an igneous rock, it requires a longer period of attack (6–8 minutes) for complete breakdown. Thus there is greater opportunity for reduction of ferric iron by organic matter during initial attack of the synthetic standard than is the case during the analysis of shales. Bearing this in mind, the agreement between calculated and determined FeO contents of the synthetic standard appears satisfactory and indicates that the method is sound in the presence of organic matter up to 4 percent carbon equivalent.

To test the precision of the method, 13 determinations were made of the FeO content of a British Coal Measure shale containing organic matter equivalent to 2.64% carbon. The values obtained were 3.42%, 3.35%, 3.30%, 3.31%, 3.45%, 3.34%, 3.41%, 3.33%, 3.40%, 3.40%, 3.38%, 3.43%, and 3.40% from which the following precision data may be calculated:

Arithmetic mean, $\bar{x}$, 3.38;
Standard deviation, S, 0.048;
Standard error, $S_{\bar{x}}$, 0.013;
Relative deviation, C, 1.42;
Relative error, E, 0.39.

There are too few determinations for these precision data to be more than an indication of the precision of the method, but they are probably sufficient to show that the method compares favourably with others commonly used for FeO determination. Mercy (1956) determined FeO by titration with potassium dichromate using diphenylamine sulphuric acid as internal indicator and obtained C values of 1.5 from 6 analyses of a granodiorite (p. 168, table 4) containing 4.3% FeO and 2.7 from 6 analyses of a granite (p. 168, table 3) containing 0.94% FeO. Fairbairn and others (1951, p. 38, table 17) quote a C value of 1.82 for determination of the FeO content by 6 analysts in one laboratory.

It appears, therefore, that the method outlined here has both accuracy and precision comparable to methods of FeO determination commonly used for rocks free from organic matter.

SOME ILLUSTRATIVE RESULTS

In order to illustrate the significance of FeO determinations in shales, the compositions of strata in a British Coal Measure cyclothem will be considered. Figure 1 shows details of the succession encountered in an underground borehole put down at Bersham colliery, North Wales. Bersham lies about 2 miles W.S.W. of Wrexham. Through the courtesy of Mr. D. Magraw of H.M. Geological Survey and the National Coal Board specimens have been made available for analysis from the levels shown. These specimens have been analysed for both major and minor (trace) constituents, but only certain constituents are given in table 1. Two points are immediately apparent from the values in this table. First, sulphide minerals are present in the lower part of the cyclothem but are insignificant in the upper (shown by the S percentages). Second, significant carbonate is present at certain levels (for example, B.C. 2, 3, and 4) but the contents of CaO are far too small for this carbonate to be calcite. The references to "ironstone" in Magraw's field notes (fig. 1) suggest that much of it may be siderite. As a first approximation the P_2O_5 contents may be assumed to be present in apatite and the CaO remaining, after P_2O_5 has been satisfied, to be present as calcite, though the amounts of Ca involved are so small that they could easily be accommodated in the clay mineral structures. CO_2 remaining after forming calcite may be assigned to siderite with the appropriate amount of FeO. It is fully realized that natural siderites frequently contain some Mg and that a slight error may be introduced by assuming that the carbonate mineral in these rocks contains none. Such an error hardly affects the total amount of carbonate mineral though it undoubtedly influences the calculated amount of FeO remaining after making siderite. The reason for making the assumption will emerge later in this discussion. S may be assigned to pyrites with the appropriate amount of Fe_2O_3 since, as pointed out earlier, iron in pyrites is reported in the analysis as Fe_2O_3. The amounts of these different compounds at different levels in the cyclothem are shown diagrammatically in figure 2.

Organic matter is present throughout the cyclothem, suggesting that reducing conditions prevailed within the sediments during the accumulation of these rocks. The low calcite contents, even assuming the $CaCO_3$ exists independently of $FeCO_3$, and the approximately equal amounts of apatite and calcite suggest that the sediments accumulated in an environment where the pH was below 7.8 and probably about 7.0 to 7.5 (Krumbein and Garrels, 1952). The cyclothem can be divided into a lower sulphide-enriched zone (below 270 ft) and an upper siderite enriched zone. The sulphide enriched zone corresponds to strongly reducing conditions in the sediment during accumulation (Eh about −0.2) while the siderite enriched zone corresponds to milder reducing conditions during accumulation (Castaño and Garrels, 1950; Krumbein and Garrels, 1952; Huber and Garrels, 1953). Thus the cyclothem strata probably accumulated in a nearly neutral environment which initially was strongly reducing but became less so as accumulation proceeded. It should perhaps be emphasized that the oxidation potentials and suggested pH

TABLE 1.—*Weight percentages of certain constituents in mudstones and other fine-grained rocks from the Bersham cyclothem*

	Fe_2O_3	FeO	CaO	Co_2	P_2O_5	S	C
B.C.1.	0.45	1.49	0.28	0.18	0.05	0.02	0.19
B.C.2.	0.53	2.72	0.28	0.70	0.15	0.02	0.29
B.C.3.	0.12	3.38	0.35	1.31	0.12	0.12	2.64
B.C.4.	0.60	3.23	0.29	1.42	0.02	0.02	0.31
B.C.5.	0.66	2.60	0.34	0.90	0.17	0.02	0.40
B.C.6.	0.60	2.35	0.46	0.56	0.12	0.03	0.39
B.C.7.	1.69	1.28	0.37	0.16	0.17	1.03	1.06
B.C.8.	1.74	1.36	0.45	0.59	0.15	0.70	1.00
B.C.9.	1.61	1.22	0.34	0.10	0.14	0.67	0.47

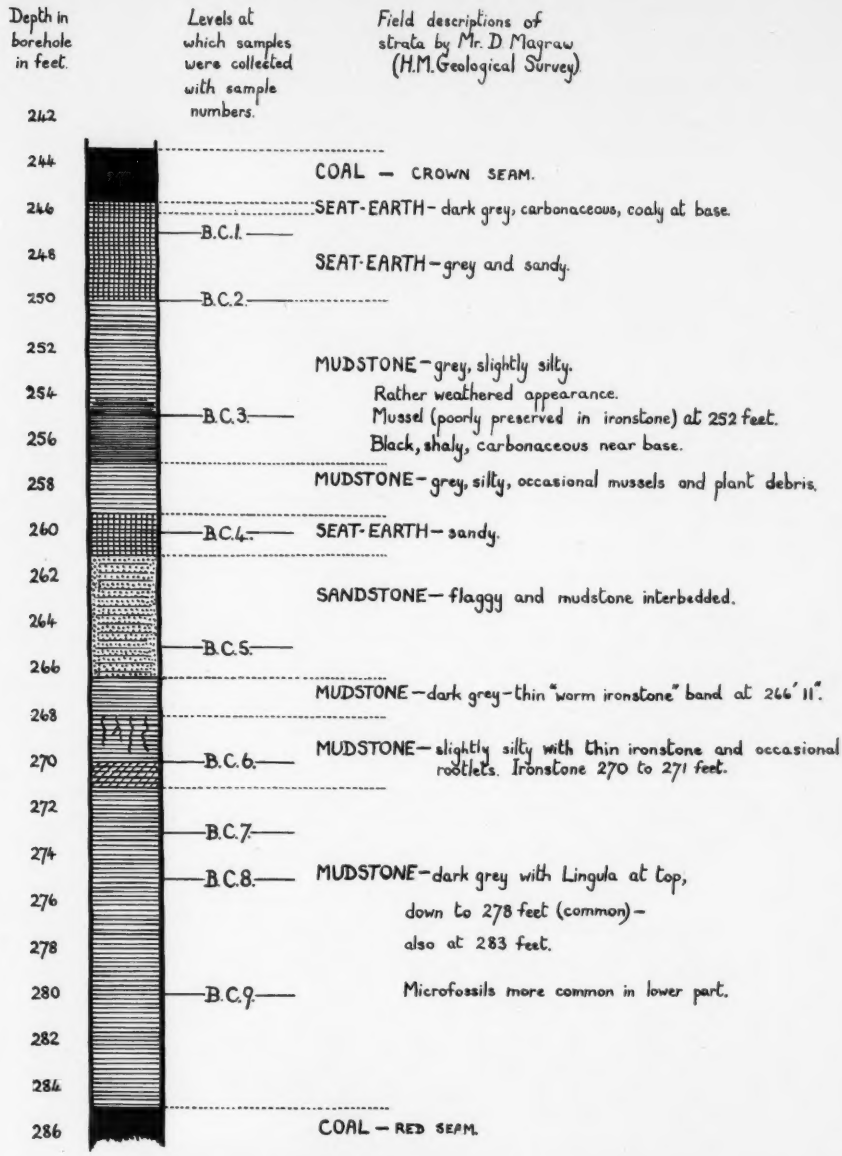

FIG. 1.—Succession in a Coal Measure cyclothem encountered in an underground borehole at Bersham colliery, North Wales. Levels from which specimens were collected for analysis are marked.

values refer to conditions within the upper part of the sediments during accumulation and not necessarily to the overlying waters.

A recent revision of the sedimentary iron mineral relationships (Huber, 1958) restricts the siderite field to lower pH and less strongly reducing conditions than those suggested above. Huber, however, stresses the limitations of his diagram and states (p. 137) that "the value of the diagram lies in its indication of the relative positions of the various stability fields rather than in their exact numerical limits on the Eh and pH scales." Being based on thermodynamic

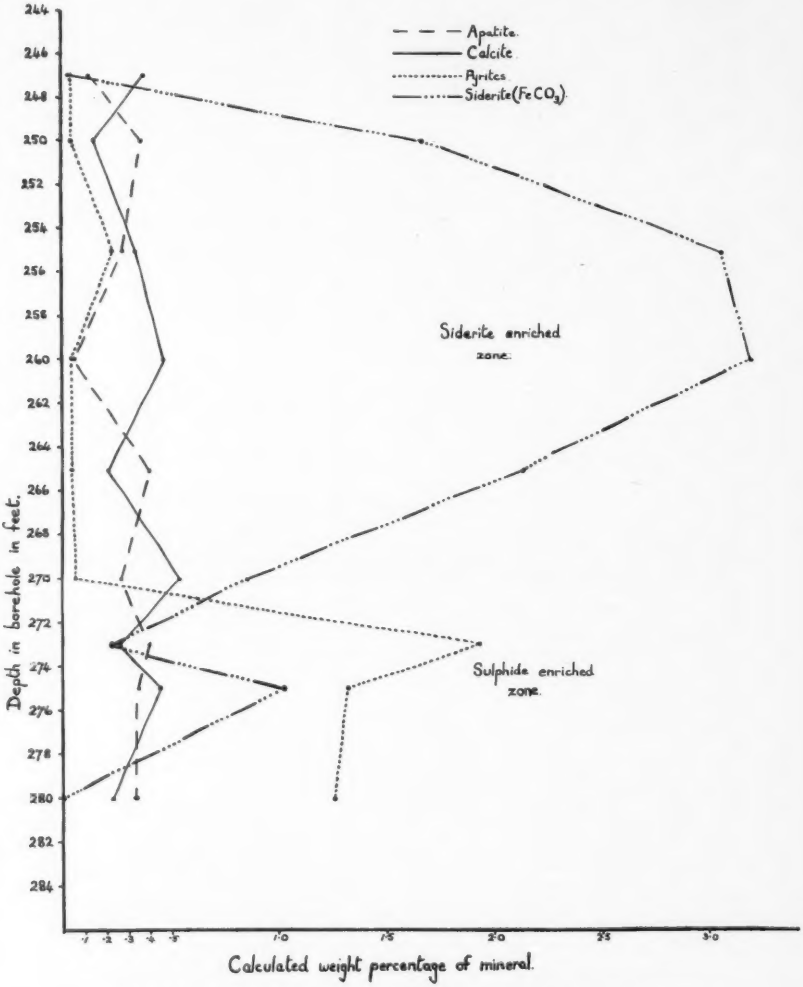

FIG. 2.—Variation of calculated mineral percentages with height in the Bersham colliery cyclothem.

calculations, it indicates the field boundaries for perfect equilibrium under the specified activity conditions. Unless perfect equilibrium is maintained, the earlier diagram of Huber and Garrels (1953, p. 352), based in part on laboratory experiment, is more likely to accord with the relationships during the accumulation of sediments. Huber's 1958 diagram then has particular value in indicating the trends which diagenetic changes would follow.

The total FeO contents of the rocks and the amounts of Fe_2O_3 remaining after forming pyrites, together with the ratio Fe^{+++} remaining/total Fe^{++}, are plotted in figure 3. It can be seen that the amounts of Fe_2O_3 remaining are higher in the lower part of the cyclothem and the values of the ratio are significantly higher there. This is surprising in view of the reducing conditions under which the lower part of the cyclothem is thought to have accumulated. In contrast, the carbonaceous-mudstone B.C. 3 contains no excess Fe_2O_3 over that required to form pyrites and the Fe^{+++}/Fe^{++} ratio at this level is zero. It might be suggested that the excess Fe_2O_3 in the lower part of the cyclothem is contained in clay minerals and the fall in the ratio Fe^{+++} remaining/total Fe^{++} as the cyclothem is ascended merely reflects the effect on this ratio of increasing amounts of siderite in the rocks at higher levels. In order to check this, the amounts of FeO remaining after forming siderite and the ratio Fe^{+++} remaining/Fe^{++} remaining have also been plotted on figure 3. The values of this modified Fe^{+++}/Fe^{++} are also higher in the lower part of the cyclothem. It will be recalled that in calculating the amounts of siderite no Mg was assigned to this mineral, that is, it was given the maximum FeO content. Thus the values for FeO remaining after forming siderite are minima and if any error has been introduced by the treatment of the analytical data it is in the direction of increasing the ratio Fe^{+++} remaining/Fe^{++} remaining in the siderite-enriched upper part of the cyclothem. The fall in this ratio in the upper part of the cyclothem cannot, therefore, be attributed to errors in the treatment of the analytical data when siderite contents were being calculated.

X-ray studies on the rocks of this cyclothem have been made by D. H. Loring. Illite and kaolinite are present throughout and small amounts of chlorite in B.C.1, B.C.2, B.C.4, B.C.5, and B.C.6 with chlorite doubtfully present in B.C.7. In the absence of information on the precise composition of the different clay minerals at the various levels it is possible, granted various assumptions, to explain the higher Fe^{+++}/Fe^{++} ratio values at the base of the cyclothem in terms of variation in the composition of clay minerals brought to the site of deposition in the solid state. But it is unsatisfactory, especially as a quite different possibility exists.

The original sulphide mineral present, particularly in the lower part of the cyclothem, may not have been FeS_2 but instead FeS or hydrotroilite ($FeS \cdot nH_2O$). Woodland (1938, p. 536–537) has suggested that the sulphide in certain mudstone bands of the Harlech Grit series was originally formed as ordinary iron sulphide (approximating to FeS) and Mohr (1955, p. 169–170) accepted this view in his examination of the same rocks. Woodland (1938) remarks that "ordinary black amorphous iron sulphide (approximating to FeS) is precipitated from solution in natural waters and it has often been recorded occurring in a finely divided state, in, for example Coal Measure shales and Rhaetic black shales." Huber (1953, p. 129) refers to several cases in the literature where forms of iron sulphide approaching FeS in composition have been reported in unmetamorphosed sedimentary rocks. The possibility that the sulphide mineral in the lower parts of the Bersham cyclothem approximated more closely to FeS than FeS_2 should therefore be considered. The Fe_2O_3 contents of the two lowest specimens analysed are, within the limits of determinative error, just sufficient to form FeS with the available S. In specimen B.C.7 the Fe_2O_3 content is insufficient and the composition of the sulphide formed by combining the available Fe_2O_3 and S is $FeS_{1.5}$ while in B.C.3 the amount of Fe_2O_3 is only sufficient to form FeS_2. At all other levels excess Fe_2O_3 remains even if FeS is formed, but the S contents are so low that the changes involved in forming FeS instead of FeS_2 are quite insignificant. Figure 4 shows the revised contents of sulphide minerals, the revised amounts of ex-

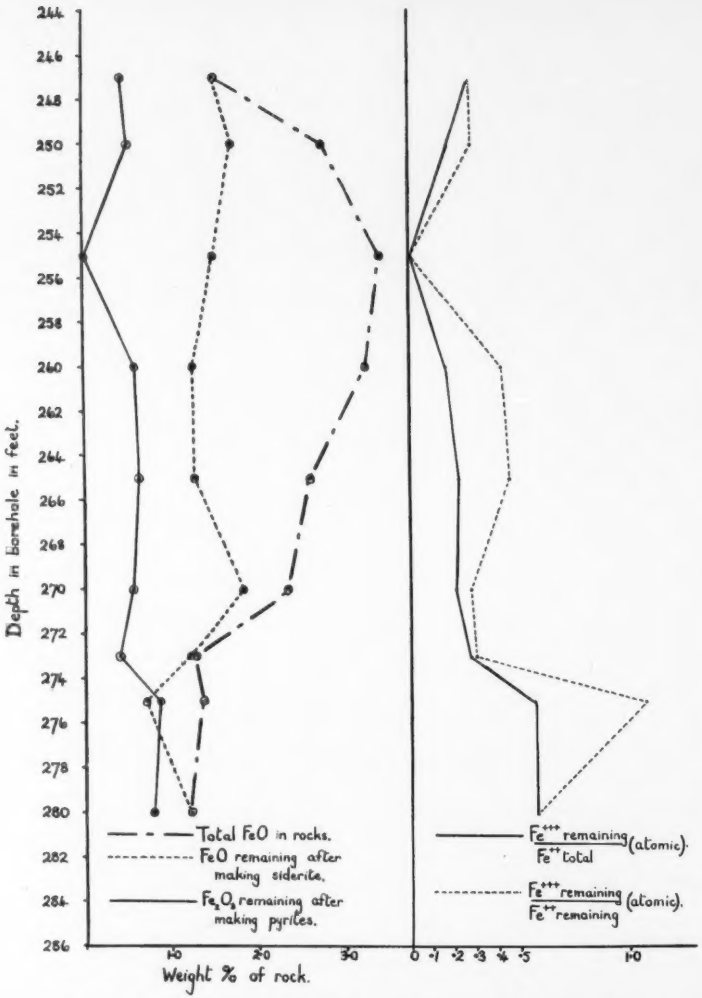

FIG. 3.—Iron content relationships in the Bersham colliery cyclothem.

cess Fe_2O_3 after forming the sulphides, the total FeO contents and the revised values for the ratio excess Fe^{+++}/total Fe^{++} at different levels in the cyclothem. With this treatment of the analytical data no sample containing significant sulphide carries any excess Fe_2O_3, while all samples in which sulphide is virtually absent have an excess of Fe_2O_3 beyond any amount that could be reasonably attributed to determinative error. A possible interpretation of this would be the precipitation of metastable ferric hydroxide under pH-Eh conditions where the stable phase is siderite (Huber and Garrels, 1953, p. 353, fig. 16) since ferric hydroxide would not precipitate under pH-Eh conditions where iron sulphide is stable. Alternatively, the iron may be brought to the site of de-

position in the ferric condition and suffer reduction there. Under the strongly reducing conditions necessary for sulphide precipitation all the ferric iron would probably be reduced, but under the mildly reducing conditions such that siderite is the stable phase, reduction of the ferric iron may not go to completion and some may become incorporated in the accumulating sediment, either in newly forming clay minerals or hydroxide. Rapid sedimentation, such as is often envisaged for the accumulation of the Coal Measure mudstones, would hinder the establishment of equilibrium and thus contribute to this effect. It is, of course, possible that the siderite is diagenetic and that the iron in the upper part of the cyclothem was originally deposited as ferric hydroxide.

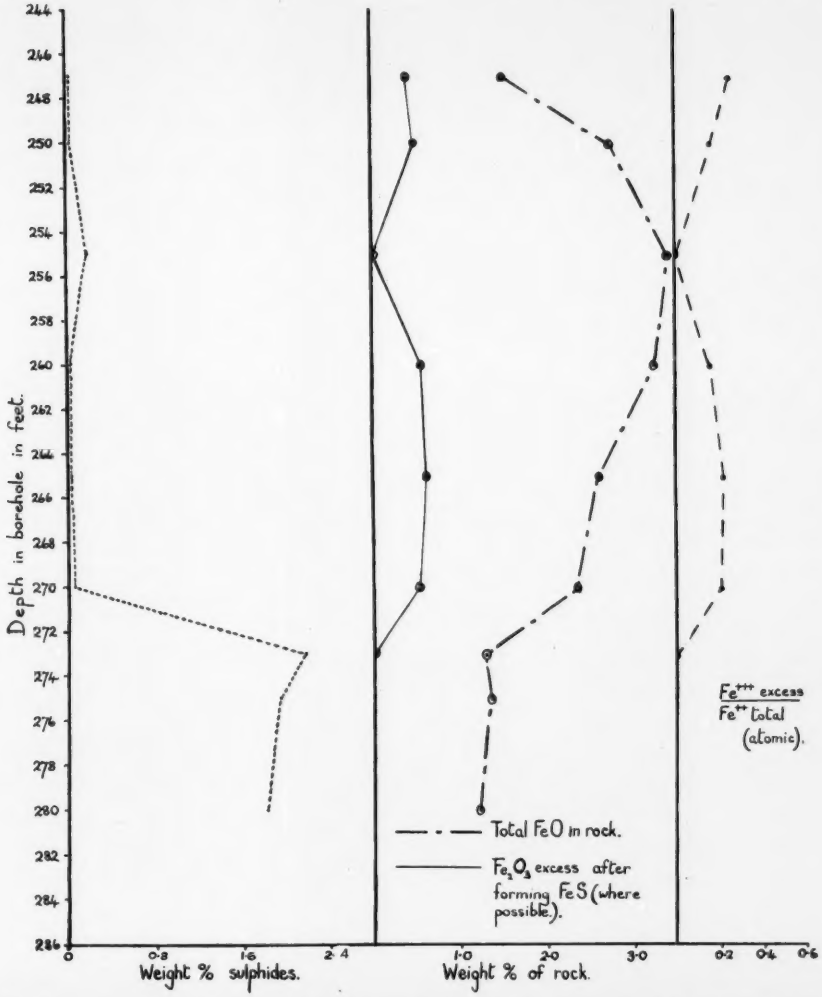

FIG. 4.—Revised sulphide contents and iron content relationships in the Bersham colliery cyclothem.

The zero Eh surface would then lie below the depositional interface during the accumulation of the upper part of the cyclothem as considered by Krumbein and Garrels (1952, p. 20, fig. 5 and text). On the other hand, comparison of the diagrams of Huber and Garrels (1953) and Huber (1958) suggests that under diagenesis siderite might be converted to hematite without any marked change in Eh and pH and this might also account for the excess Fe_2O_3 in the siderite enriched zone. It is not possible from the chemistry alone to distinguish between these alternatives, but whichever is correct leaves unchanged the sequence of variation in conditions during the accumulation of the cyclothem, namely a fall in the level of the zero Eh surface relative to the depositional interface as accumulation proceeded.

The supposition that the sulphide mineral at the lower levels was FeS raises a further point of minor interest. James (1954, p. 241) refers to the uncertainty attaching to the boundary between the siderite and pyrite fields in the diagram by Krumbein and Garrels (1952) in that the value used for the activity product of pyrites in the calculation is actually that of FeS. If, in fact, the sulphide forming was FeS this uncertainty is removed.

Finally, it may be pointed out that discussions such as that attempted here depend on determinations of the FeO contents of the shales. By the method suggested in this paper such determinations can be achieved with reasonable precision and accuracy even when significant amounts of organic matter are present.

REFERENCES

Belcher, R., and Wilson, C. L., 1956, New methods in analytical chemistry. 2nd (revised) impression, Chapman and Hall, London, 304 p.

Castaño, J. R. and Garrels, R. M., 1950, Experiments on the deposition of iron with special reference to the Clinton iron ore deposits: Econ. Geology, v. 45, p. 755–770.

Fairbairn, H. W., 1953, Precision and accuracy of chemical analyses of silicate rocks: Geochim. et Cosmochim. Acta, v. 4, p. 143–156.

Fairbairn, H. W., and others, 1951, A co-operative investigation of precision and accuracy in chemical, spectrochemical and modal analysis of silicate rocks: U. S. Geol. Survey Bull. 980.

Groves, A. W., 1951, Silicate analysis. 2nd ed. George Allen and Unwin, London, 336 p.

Heisig, G. B., 1928, Volumetric determination of ferrous iron by means of potassium iodate: Jour. Am. Chem. Soc., v. 50–1, p. 1687–1691.

Hey, M. H., 1949, Analytical notes II: the 'ferrous iron' and silica determinations in rocks and minerals (abs.,): Am. Mineralogist, v. 34, p. 769.

Hillebrand, W. F., Lundell, G. E. F., Bright, H. A. and Hoffman, J. I., 1953, Applied inorganic analysis with special reference to the analysis of metals, minerals and rocks. 2nd ed., John Wiley and Sons, Inc., New York, 1034 p.

Hirst, D. M. and Nicholls, G. D., 1958, Techniques in Sedimentary Geochemistry: (1) Separation of the detrital and non-detrital fractions of limestones: Jour. Sedimentary Petrology, v. 28, p. 468–481.

Huber, N. K., 1958, The environmental control of sedimentary iron minerals: Econ. Geology, v. 53, p. 123–140.

Huber, N. K. and Garrels, R. M., 1953, Relation of pH and oxidation potential to sedimentary iron mineral formation: Econ. Geology, v. 48, p. 337–357.

James, H. L., 1954, Sedimentary facies of iron-formation: Econ. Geology, v. 49, p. 235–293.

Krumbein, W. C. and Garrels, R. M., 1952, Origin and classification of chemical sediments in terms of pH and oxidation-reduction potentials: Jour. Geology, v. 60, p. 1–33.

Mercy, E. L. P., 1956, The accuracy and precision of "rapid methods" of silicate analysis: Geochim. et Cosmochim. Acta, v. 9, p. 161–173.

Mohr, P. A., 1955, A geochemical study of the Lower Cambrian Manganese Shale group sediments of the Harlech Dome. Unpub. Ph.D. thesis, University of Manchester.

Mueller, G., 1954. The theory of genesis of oil through hydrothermal alteration of coal type substances within certain Lower Carboniferous strata of the British Isles: Comptes Rendus de la dix-neuvieme session, Congrès Gèologique International, fasc. XII, p. 279–328.

O'Neil, R. L., 1959, Analytical procedures applicable to fine-grained sedimentary rocks: Jour. Sedimentary Petrology, v. 29, p. 267–280.

Smith, G. F. and Wilcox, C. S., 1942, New indicators for iodate-iodine monochloride Andrews analytical procedures: Ind. Eng. Chem. Anal., v. 14, p. 49–53.

Washington, H. S., 1930, The chemical analysis of rocks. 4th ed., John Wiley and Sons, Inc., New York, 296 p.

Woodland, A. W., 1938, Some petrological studies in the Harlech Grit series of Merionethshire. III. The development of pyrite in the grits and mudstones: Geol. Mag., v. 75, p. 529–539.

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FIGS. 1–4, DECEMBER, 1960

DETERMINATION OF CO_2 IN CARBONATE ROCKS BY CONTROLLED LOSS ON IGNITION[1]

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ABSTRACT

A method which uses a controlled loss on ignition for the determination of CO_2 in carbonate rocks was developed to provide a simple and reliable means of producing results from a group of samples at the same time. The routine loss on ignition was modified slightly to include two steps instead of one. A loss at 550° C is recorded as well as the loss at 1000° C. Thus, by accurately controlling the temperature, values were obtained for the carbonate and non-carbonate portions of the loss on ignition. The method is demonstrated to be rapid and as reliable as acid evolution methods. Differential thermal analysis technique was used to aid in time and temperature selections. DTA curves, experimental data, and procedures are shown.

INTRODUCTION

Combustion or acid evolution with gas absorption have long been recognized as two excellent methods for the determination of carbon dioxide (Griffen, 1949; Hillebrand, 1919; Willard and Furman, 1940). One of the deficiencies of these methods is that they are limited to one determination at a time for each absorption train available. The possibility of determining the carbon dioxide content of a group of samples provided the stimulus for a study using a loss on ignition technique adapted for this purpose. Work was begun on the problem in 1954; a method has been in use since early 1955, with additional refinements being made as new knowledge of the method and skill in using it were acquired.

The loss on ignition has been a part of routine analysis for many years, and when reported as a net loss of weight after ignition, it will provide a summation near 100 percent where the other elements are reported as their normal oxides. A loss on ignition may be used as an approximation of carbon dioxide when applied to high calcium limestones and will be very near the true carbon dioxide value as determined by combustion or acid evolution methods. This ignition loss determination breaks down, however, when applied to impure limestones because of the carbonaceous material and other volatiles present. Because of the type of equipment needed and the time involved, acid evolution with gas absorption methods of CO_2 analysis are many times impractical for small laboratories. A controlled loss on ignition method was devised, therefore, as a means of providing a simple, reliable method of carbon dioxide analysis on a group basis without the addition of extra specialized laboratory equipment.

LABORATORY INVESTIGATION

The initial problem of the study was to establish critical temperatures and times for carbonate and non-carbonate losses. Different types of carbonate rocks and reagent grade calcium carbonate (fig. 1) were analyzed by differential thermal analysis to establish approximate temperature of reaction. Bureau of Standards sample number 1a, an argillaceous limestone (fig. 2), was used as the principal standard because it best represented the type of carbonate samples normally analyzed by this laboratory. D.T.A. showed the temperature at which carbon dioxide began to evolve was between 400° C and 600° C. Once this range was established, further experimental work was carried out with a laboratory muffle furnace equipped with a temperature control unit which regulated the temperature to within +20° C and −15° C of the selected temperature.

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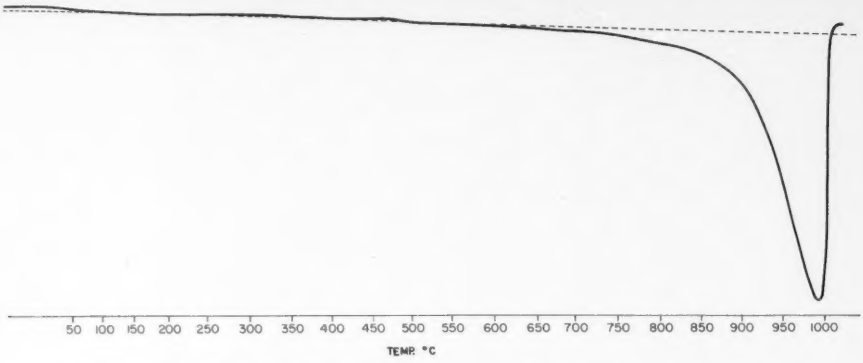

FIG. 1.—Differential thermal analysis curve of reagent grade calcium carbonate. (Dotted line represents projected base line.)

First experiments which involved the use of the muffle furnace centered around the possibility of dividing the loss on ignition into separate determinations for carbonaceous material, other non-carbonate volatiles, and carbon dioxide. However, after extensive work with a wide variety of samples, including calcareous shales and dolomitic limestones, it was found impractical to make separate determinations for non-carbonate and carbonaceous material. D.T.A. curves gave indication that such a separation might be possible (fig. 2), but when an attempt was made to establish a definite temperature at which all carbonaceous material was evolved, erratic results were often obtained. It was then decided to divide the loss on ignition into two determinations, one for carbon dioxide from carbonate minerals and the other for all non-carbonate volatiles.

After extensive experimentation with various temperatures between 400° C and 600° C, 550° C was found to be the optimum temperature at which carbon dioxide could be retained while other volatiles were evolved. Twenty-five minutes was determined to be the maximum time needed for the evolution of carbonaceous material and hydrated water.

The entire procedure may be summarized

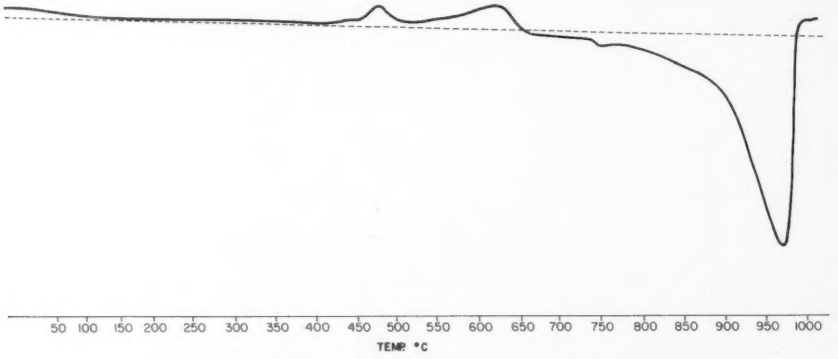

FIG. 2.—Differential thermal analysis curve of Bureau of Standards Sample No. 1a. (Dotted line represents projected base line.)

briefly in the following manner:

1. Samples were ground to a grain size of 100 percent passing a 60-mesh sieve.
2. A 2-gm sample was weighed into a platinum crucible and dried for one hour at 105° C; dried weight was recorded (all results were based on dried weight at 105° C).
3. Samples were placed in a muffle furnace which had been heated to 550° C, left for exactly 25 minutes, removed, cooled and weighed, and percent loss recorded.
4. Samples were returned to muffle furnace which was held at 550° C and the temperature increased to 1000° C.
5. Samples were left in furnace at 1000° C for one hour, then removed, cooled and weighed, and the percent CO_2 lost recorded.

Table 1 shows a comparison between the average of 12 determinations made on BS-1a using the above procedure and the average as listed on the Bureau of Standards certificate of analysis. A comparison is also shown between the range of the 12 determinations made by this laboratory and the determinations listed by the Bureau of Standards. An explanation of the value given for the percent loss at 550° C under the column "Average as listed by Bureau of Standards" is in order. Because the Bureau of Standards does not list a determination of this type, this value was obtained by taking the difference between the average values of the loss on ignition and the CO_2 as listed on the certificate.

The calculations relied upon to supplement the experimental results obtained with BS-1a are some of the facts which bear upon the method just discussed. We assumed the most simple conditions possible for the calculations, that is, we computed all of the carbon dioxide to carbonate. Correction was made for the amount of calcium oxide present as gypsum and apatite, and the remainder was computed as calcium carbonate. Magnesium was utilized to convert the remainder of carbon dioxide to carbonate. Where the percentages of non-carbonate material such as silica and alumina indicated clay minerals present, the remainder of the magnesium was assumed to be in this form.

Calculations may be made in the following manner:

Sample #KGS-58230 (The Bethany Falls Limestone) is analyzed and found to contain:

41.27%	CO_2
51.29%	CaO
1.17%	MgO
0.05%	SO_3
0.04%	P_2O_5

A small amount of CaO is assumed to be in the form of gypsum and apatite and is calculated as such from the percentages of SO_3 and P_2O_5 using these gravimetric factors:

$$\frac{CaSO_4 \cdot 2H_2O\ (MW)}{SO_3\ (MW)} = 2.15013$$

$$0.05 \times 2.15013 = 0.11\%\ SO_3 \text{ as gypsum.}$$

$$\frac{3[Ca_3(PO_4)_2] \cdot CaF_2\ (MW)}{3P_2O_5\ (MW)} = 2.36846$$

$$0.04 \times 2.36846 = 0.09\%\ P_2O_5 \text{ as apatite.}$$

$$\frac{CaO\ (MW)}{CaSO_4 \cdot 2H_2O\ (MW)} = 0.32571$$

$$0.11 \times 0.32571 = 0.04\%\ CaO \text{ as gypsum.}$$

$$\frac{10CaO\ (MW)}{3[Ca_3(PO_4)_2] \cdot CaF_2\ (MW)} = 0.5559$$

$$0.09 \times 0.5559 = 0.05\%\ CaO \text{ as apatite.}$$

The two values for CaO as gypsum and CaO as apatite are then subtracted from the calcium oxide value obtained by analysis to give the value for calcium oxide present as calcium carbonate:

$$51.29 - 0.04 - 0.05 = 51.20\%\ CaO$$

Calcium carbonate is then computed from this value:

$$\frac{CaO\ (MW)}{CaCO_3\ (MW)} = 0.5603$$

$$\frac{51.20}{0.5603} = 91.38\%\ CaCO_3$$

$$91.38 - 51.20 = 40.18\%\ CO_2$$

consumed as $CaCO_3$.

$$41.27 - 40.18 = 1.09\%\ CO_2$$

which is assigned to MgO as $MgCO_3$.

Magnesium carbonate is then computed:

$$\frac{MgO\ (MW)}{MgCO_3\ (MW)} = 0.5219$$

$$\frac{1.09}{0.5219} = 2.09\%\ MgCO_3$$

TABLE 1.—*Loss on ignition determinations on BS-1a*

	Average of 12 runs	Range of Samples run by Kansas Geological Survey	Average as listed by Bureau of Standards	Range of Samples as listed by Bureau of Standards
% loss @ 550° C	0.93	0.79 to 1.13	1.02	———
% loss @ 1000° C-CO_2	33.46	33.22 to 33.60	33.53	33.36 to 33.65
Total loss	34.39	34.15 to 34.46	34.55	34.49 to 34.60

The mean deviation of percentage for the loss at 1000° C, or CO_2, as determined by the authors is 0.10 percent. The mean deviation of percentage for the CO_2 values listed by the Bureau of Standards is 0.08 percent. The CO_2 values listed on the Bureau of Standards certificate of analysis were obtained by using the acid evolution with gas adsorption method of analysis. The total loss on ignition values also show good agreement. The mean deviation for the 12 samples of BS-1a run by the authors is 0.04 percent, while the mean deviation for the ten samples listed by the Bureau of Standards is 0.03 percent.

In this particular sample, there is an excess of 0.17 percent magnesium oxide which is not consumed as magnesium carbonate and may be assigned to the small amount of clay minerals which are indicated to be present by the small percentage of non-carbonate materials as determined by analysis.

When the mineral calculations consumed the chemical compounds reported by analysis, and where the analysis summation was close to 100 percent, a correct analysis was assumed.

The procedure has proved quite successful for most of the work which has been done in the Kansas Geological Survey laboratory, with two exceptions. Where material being analyzed contains more than trace amounts of kaolinite or montmorillonite clay minerals, hydrated water given off above 550° C interferes. If finely ground dolomite is present, carbon dioxide is evolved below 550° C. Additional work with dolomitic limestones indicates that reliable results can be obtained by using the controlled loss on ignition method if the grain size is limited to 100 percent passing a 60-mesh sieve. Figure 3 shows a D.T.A. curve for BS-88 (a pure dolomite) which is ground to at least the 100-mesh size. The curve indicates the evolution of carbon dioxide beginning slightly below 500° C. Figure 4 shows a D.T.A. curve for a sample taken from a naturally

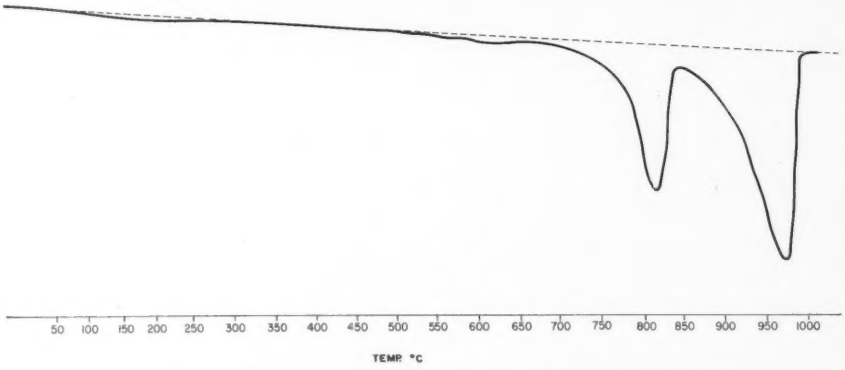

FIG. 3.—Differential thermal analysis curve of Bureau of Standards Sample No. 88. (Dotted line represents projected base line.)

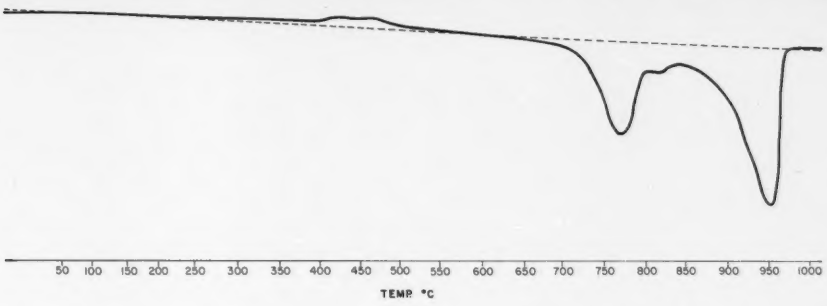

FIG. 4.—Differential thermal analysis curve of Kansas Geological Survey Sample No. 598. (Dotted line represents projected base line.)

occurring dolomite (KGS #598) which was ground to the 60-mesh size. This curve indicates the evolution of carbon dioxide beginning at a temperature just above 600° C. Because of the lack of additional dolomitic samples from known standards, extensive experimental work has not been done to conclusively prove or disprove this observation. Additional study and investigation will be made as more samples become available. The third exception is limestone which contains large amounts of pyrite or FeS_2, large amounts meaning 0.2 percent or more. The oxidation of FeS_2 to Fe_2O_3 and SO_3 causes a gain in weight (Kolthoff and Sandell, 1946) which produces an error in the CO_2 determination when using the controlled loss on ignition method. Additional work has been done in the Geochemistry Laboratory of the Kansas Geological Survey to provide an alternate method for the determination of CO_2 in pyritic limestones by controlled loss on ignition (Waugh and Hill, 1960).

SUMMARY

As a rapid, accurate method of determin-

TABLE 2.—*Routine determinations and calculation of CaCO₃ and MgCO₃ on five naturally occurring limestones and BS-1a*

Sample	K.G.S. #57245 Farley Ls.	K.G.S. #58254 Plattsmouth Ls.	K.G.S. #58233 Winterset Ls.	K.G.S. #58308 Toronto Ls.	K.G.S. #58249 Toronto Ls.	Average of 4 determinations on BS-1a.
% CO_2	42.69	39.01	39.43	38.23	26.55	33.43
% All other volatiles	0.35	0.74	0.61	1.69	2.22	0.91
% CaO	53.31	49.17	48.54	40.41	33.07	41.57
% MgO	0.88	0.57	1.61	6.12	1.01	2.11
% All other elements demined	2.43	10.16	9.31	13.49	36.64	21.44
Total	99.60	99.65	99.50	99.94	99.49	99.46
% Calculated $CaCO_3$	95.02	87.56	86.45	71.03	58.83	73.73
% $MgCO_3$	1.74	0.98	2.64	12.65	1.30	1.94

Note: "Percent all other elements" includes silica, alumina, total iron as Fe_2O_3, titania, and potassium and sodium oxides.

ing carbon dioxide, the controlled loss on ignition method has given excellent results for the type of work done in the Kansas Geological Survey laboratory. Study has shown that where proper sampling techniques and clean samples are used and all the conditions discussed in this paper are met, the results obtained will be as reliable and reproducible as results produced with acid evolution methods. The CO_2 results were assumed to be correct when the entire amount of carbon dioxide was consumed in the calculation of all the calcium and magnesium oxides to their carbonate equivalents. The ability to get reproducible results on a sample where the amount of CO_2 is known (BS-1a) also helped to establish confidence in the method.

Table 2 shows carbon dioxide and other volatiles determined by loss on ignition, calcium and magnesium values, and the calculated percentages of calcium and magnesium carbonate from the analyses of five naturally occurring limestones. The values shown in this table indicate that the method has been used on samples with various degrees of purity. Purity, in this case, is indicated by the percentage of calcium and magnesium carbonate shown to be present by calculation. As shown in the table, good results have been obtained on samples with as high as 95 percent and as low as 59 percent calcium carbonate. Sample #58308 (Column 4) shows a small amount of dolomite to be present as indicated by the larger amount of magnesium carbonate. This is further indication that the procedure may be used where dolomite is present if the sample is ground to a grain size small enough to just pass a 60-mesh sieve.

At first glance the method may seem to be restrictive in its use, but experience has shown that if care is used in its manipulation, acceptable results will be obtained on a wide variety of samples. The fact that carbon dioxide may be determined from a group of samples at the same time only serves to increase the importance of the use of this method where conditions permit.

REFERENCES

GRIFFEN, C. W., 1949, Inorganic quantitative analysis. The Blakiston Co., Philadelphia, 368 p.

HILLEBRAND, W. F., 1919, The analysis of silicate and carbonate rocks: U. S. Geol. Survey Bull. 700, 285 p.

KOLTHOFF, I. M., AND SANDELL, E. B., 1946, Textbook of quantitative inorganic analysis. The Macmillan Co., New York, 794 p.

WAUGH, W. N., AND HILL, W. E., 1960, Determination of carbon dioxide and other volatiles in pyritic limestone by loss on ignition: Jour. Sedimentary Petrology, v. 30, p. 144–147.

WILLARD, H. H. AND FURMAN, N. H., 1940, Elementary quantitative analysis. D. Van Nostrand Co., Inc., New York, 531 p.

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NOTES

MOUNTING HEAVY MINERAL GRAINS[1]

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The conventional method of mounting heavy mineral grains is very cumbersome. In the course of his studies of Burmese Tertiary sandstones, the author developed a new technique for mounting mineral grains. This technique, which is described below, simplifies and speeds the preparation of permanent mounts of heavy mineral grains.

The necessary amount of Canada balsam is put on a slide, which is then heated slightly to melt the balsam. Heavy mineral grains are placed in the melted balsam and covered by a cover slip. A little practice makes it possible to prepare such mounts with an even distribution of grains devoid of air bubbles. The slide is then placed in an air heated oven, pre-heated to 65° C, and left for approximately 6 to 8 hours. The slide should be removed from the oven before the Canada balsam turns yellow. On cooling, a permanent mount is thus obtained.

Three precautions are necessary: (1) The temperature in the oven should not be allowed to exceed 70° C, because at high temperature balsam begins to froth. The author obtained the best results cooking the balsam slowly at temperatures between 65° and 70° C. (2) After emplacement of the cover slip, a little balsam should be spread along the edges of the cover glass before the slide is placed in the oven. On heating expansion causes the cover slip to rise, and if there is no balsam to move in from the edges air bubbles move in. (3) Over-cooking and under-cooking of the balsam should be avoided. A little experience enables one to decide the stage at which further cooking of the balsam is to be stopped.

Using this technique, the author was able to prepare 60 to 80 slides of heavy mineral grains at one time and then place them all in an air oven for preparation of permanent mounts.

[1] Manuscript received June 2, 1960.

MINERALOGICAL ANALYSIS OF CARBONATE ROCKS BY X-RAY DIFFRACTION[1]

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INTRODUCTION

It is often difficult to distinguish calcite, dolomite, and siderite in polished- or thin-section studies. Normal laboratory procedure in identifying carbonate rocks is generally based on (1) the degree of effervescence in cold dilute acid, (2) selective staining tests, (3) optical properties, or (4) variance in specific gravity. The shortcomings of the above tests are well known: they are not reliable, are time consuming, or make it necessary to destroy a rock specimen which may be needed for petrologic studies of texture or fabric.

The use of the X-ray diffractometer provides a quick method for establishing the

[1] Published by permission of the Chief, Illinois State Geological Survey. Manuscript received November 15, 1959.

presence of calcite, dolomite, and siderite in carbonate rocks. Further, clay minerals or other common mineral constituents of carbonate rocks can also be identified if present in sufficient quantities.

PROCEDURE

A rock slice is cut so that it will fit into the slide holder of the diffractometer used. The surface to be examined is ground smooth with #600 carborundum powder and polished with stannic oxide or cesium oxide. Suitable results can generally be obtained after grinding with the #600 carborundum, but the recorded X-ray reflections will likely be less pronounced (lower intensity) than reflections from a highly polished surface. Used slices are available for subsequent completion of thin sections.

Several hundred polished sections of the Lower Cretaceous Georgetown Limestone collected in Val Verde County, Texas, were analyzed in a General Electric XRD-3 X-ray diffractometer, using copper radiation. A 3° slit was used in order to irradiate a moderately representative field; goniometer speed was set at 2° per minute. The X-ray reflections were recorded by a Leeds and Northrup speedomax unit. The rock-forming carbonates and their associated minerals can be detected by scanning from 20° to 35°–2θ. Therefore, the type of carbonates can be identified in 8 minutes. A rock slice is cut approximately three-tenths (0.3) of an inch thick and trimmed to a width of one inch and length of one to three inches so that it will fit into the slide holder of the General Electric diffractometer.

Thin sections may be analyzed in the same manner as polished sections but do not produce comparable results in that a large percentage of X-rays pass through the slide rather than reflect from the thin-section surface. The intensity of the reflections is therefore greater from the more opaque surface of the polished sections. If thin sections are analyzed by this method the cover glass must be removed.

Examination of argillaceous carbonates has shown good results for the identification of the clay minerals present. As most of the clay minerals are composed of sheet structures similar to mica, more pronounced reflections are obtained by cutting the rock section parallel to the bedding.

In multicomponent rocks for which any diagnostic reflections are coincident the analysis may still be conducted by extending the range of the diffraction angles.

Where it is necessary to identify minerals other than carbonates which are present in quantities of less than 5%, the rock sample is digested in a dilute solution of glacial acetic acid to concentrate the insoluble residue. The insoluble residue may then be placed on a petrographic glass slide for analysis in the same manner as clay minerals are prepared.

TABLE 1.—*Common carbonates and associated minerals which have a strong diffraction effect between 20° and 35° 2θ*

Mineral	Degrees 2θ (copper radiation)
Calcite	29.4°
Dolomite	30.6° to 30.9°
Siderite	31.5° to 32.0°
Kaolinite	24.9°
Illite (hydrous mica)	26.7°
Montmorillonite	19.5° to 20.0°
Quartz	26.6°
Gypsum	23.3° and 29.0°
Anhydrite	25.4°
Barite	25.9°
Pyrite	33.0°
Hematite	33.2°
Goethite	22.0° and 33.2°
Fluorite	28.3°
Halite	31.7°

RESULTS

A list of common carbonates and associated minerals with their strongest 2θ reflections is shown in table 1. The reflections obtained are based on the crystal structure, and therefore the data obtained are unequivocal unless two or more minerals produce reflections at the same 2θ position. From the present study it appears that minerals present in polished carbonate sections in quantities greater than 5% can be easily detected. In favorable cases smaller percentages of a mineral can be detected. Quartz, which has a good scattering effect, can be detected in quantities less than 5% of the total rock surface being examined.

Selected diffractometer traces of the Georgetown Limestone are shown in figures 1 and 2. By referring to the 2θ reflections

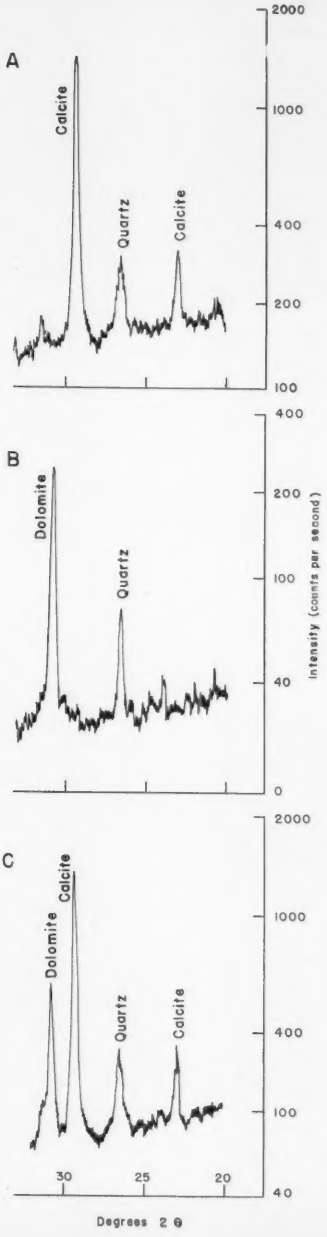

FIG. 1A.—Limestone with minor amount of quartz.
1B.—Dolomite with some quartz.
1C.—Dolomitic limestone containing some quartz.

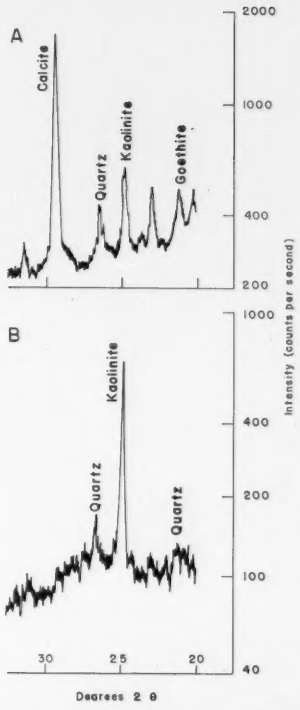

FIG. 2A.—Argillaceous limestone with minor amounts of kaolinite, quartz, and goethite.
2B.—The insoluble minus 2 micron fraction of the above limestone after digestion in glacial acetic acid.

given in table 1, the first trace (fig. 1A) is identified as a limestone containing a minor amount of quartz. The second trace (fig. 1B) is a dolomite containing some quartz, and the third (fig. 1C) is a dolomitic limestone.

Figure 2 shows two traces from an argillaceous limestone; the first (fig. 2A) was recorded from a polished surface and the second (fig. 2B) consists of the minus 2 micron fraction after digesting the carbonate in a dilute solution of glacial acetic acid. The polished section recorded a limestone containing minor amounts of kaolinite, quartz, and goethite, whereas the minus 2 micron fraction (b) shows a predominant reflection for kaolinite with a small quantity of quartz. Concentration of the kaolinite by removing the carbonate has increased the intensity of its reflection several times.

The use of X-ray diffractometer traces is of particular value in the identification of the minerals present in carbonate rocks when a large number of samples, such as measured stratigraphic sequences, are to be analyzed. The above described method is quick, and the results have the least possible chance of being misinterpreted.

For fine-grained rocks not subject to erratic incidence of strong reflection from any single large grain, the method can be extended to semiquantitative or quantitative estimates of abundance of the several components.

OUTGROWTHS OF AUTHIGENIC BROOKITE ON LEUCOXENE GRAINS IN PENNSYLVANIAN AND LATE MISSISSIPPIAN SANDSTONES OF INDIANA[1]

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Outgrowths of authigenic brookite on leucoxene grains occur in sandstones of Pennsylvanian and late Mississippian age which crop out in a north-south belt in southwestern Indiana. Table 1 shows the number of sandstone samples examined from each formation. All the sandstones are well sorted and mature and contain more than 85 percent quartz. The heavy mineral fraction (sp. gr. greater than 2.95) constitutes less than 0.5 percent of a sample. Iron oxides, leucoxene, zircon, tourmaline, and rutile are the chief constituents in decreasing order of abundance in the heavy fractions.

TABLE 1.—*Number of sandstone samples examined from each formation*

Age	Formation	Number of samples examined
Pennsylvanian	Merom Sandstone	8
	Dugger	7
	Petersburg	6
	Linton	10
	Staunton	6
	Mansfield	20
Late Mississippian	Tar Springs	12
	Big Clifty	18
	Sample	4

The leucoxene is milky, grayish, or yellowish white and may be irregular and ragged, cryptocrystalline, or smooth and well rounded. The cryptocrystalline variety has yellow elongate microlites which are barely translucent. The other varieties are opaque and may have a small core of ilmenite. The leucoxene grains do not exceed 0.1 mm in maximum dimension. Identity of leucoxene was confirmed by spectrochemical analyses that showed titanium as a major constituent. Weak lines on X-ray patterns indicate that the microlites in the cryptocrystalline leucoxene are brookite. X-ray patterns of noncryptocrystalline leucoxene contain no distinct lines.

[1] Published by permission of State Geologist, Indiana Department of Conservation, Geological Survey. Manuscript received November 23, 1959.

FIG. 1.—Outgrowths of authigenic brookite on leucoxene. ×300. Clear brookite crystals are protruding from opaque leucoxene masses.

Square to rectangular euhedral crystals of brookite project outward from all varieties of leucoxene (fig. 1). The brookite outgrowths are colorless or yellow and are rarely weakly pleochroic. Very high refractive indices (above 2.20), a biaxial interference figure with a small 2V, and very strong dispersion (giving rise to spectral colors on rotation of the microscope stage with the nicols crossed) identify the mineral. The brookites have striations parallel to the longer dimension and truncated edges; crystals do not exceed 0.075 mm in maximum dimension and average approximately 0.04 mm. The brookite projections are sparse but occur in all samples examined. Individual nonattached brookite euhedra are found in all the sandstones and possess the same characteristics as the attached variety. The mechanical breaking off of a brookite projection from a leucoxene grain produced these individuals.

McCartney (1931, p. 85) observed these brookite projections in some late Mississippian sandstones of Indiana, but Tyler and Marsden (1938, p. 55) could not find brookite in McCartney's samples.

The brookite described above grew from the leucoxene. Brookite microlites grew into large crystals which eventually protruded outward from a leucoxene grain. Tyler and Marsden (1938, p. 57) observed compound grains of leucoxene and rutile and leucoxene and anatase and proposed the aforementioned microlite-growth origin for the rutile and anatase. These authors did not observe compound grains of leucoxene and brookite but postulated that perhaps brookite could form in the same manner as anatase and rutile.

REFERENCES

McCARTNEY, G. C., 1931, A petrographic study of the Chester sandstones of Indiana: Jour. Sedimentary Petrology, v. 1, p. 82–90.

TYLER, S. A., AND MARSDEN, R. W., 1938, The nature of leucoxene: Jour. Sedimentary Petrology, v. 8, p. 55–58.

A CARBONATE VEIN IN LIMESTONE[1]

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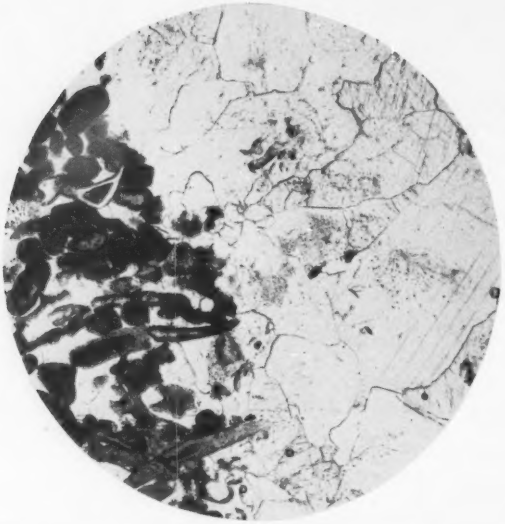

FIG. 1.—Photomicrograph of a calcite vein (×15). Replacement is observed at the contact of the vein with the unreplaced rock at the left of the photograph. The latter is composed predominantly of fossils and their fragments. The crystals of calcite in the vein are larger than those of the original rock fragments.

In order to gain an understanding of the history of carbonate veins, a small vein from the Salem Limestone of Indiana was studied in thin-sections and analyzed spectrographically. Most of the vein is coarsely granular. Recrystallization may be more pronounced in some parts than in others, and there is difficulty in establishing the primary or secondary nature of the calcite. Spectrographic analyses were run on the following samples:

1.—Foraminifera of the Endothyroid type, relatively free from the matrix externally but filled internally, collected at the Old Cleveland Quarry.

2.—A small fragment of limestone including fossils and calcite cement, a very "typical" fragment of Salem Limestone.

3.—Calcite crystals, visible to the naked eye, from the intergrain spaces, isolated under the microscope.

4.—Fragments of relatively opaque, pure calcite crystals from the calcite vein (fig. 1).

The four samples are believed to represent different stages in the development of the rock. Foraminifera were deposited first, and the intergranular crystals of calcite and the vein obviously are later. The rock fragments are a mixture of original calcareous sediments and cement.

The samples analyzed are all fairly uniform in composition. Magnesium in (3) may indicate a small amount of dolomite which, however, was not detected optically. The high values of iron and silica obtained for Foraminifera (1) may be explained by a state of weathering of the rock involving slight enrichment.

In marine shells, calcite appears to have

[1] Manuscript received November 24, 1959.

a high magnesium content; this is especially true for Foraminifera. These materials are unstable at earth-surface temperature and pressure. Calcite, thermodynamically stable at low temperature, is almost free of magnesium according to Goldsmith, Graf, and Joensuu (1955). Thus, if organically-derived calcareous sediments are low in magnesium (less than 1.0 percent), it is very probable that magnesium has been removed.

Since the analyzed samples do not show any considerable or consistent compositional differences, one may assume that the rock has approached a state of equilibrium consistent with the pressure and temperature at diagenesis and that the original nature of the sediments has been changed. It is safe to say that magnesium has been removed from the fossil shells (Chave, 1954) as has a large part of the organic matter. The matrix shows a composition strikingly similar to that of the fossils. Although the differences appear to be very small, the vein (4) seems to be composed of the purest calcite of the four samples analyzed. This possibly would also be the case with sample (3)—individual calcite crystals—if one could separate them completely from the surrounding matrix which may also contain other elements. Samples 3 and 4 are products of diagenetic processes.

Examination of figure 1 reveals that this is a replacement vein. Ghosts of the original grains are present, which clearly indicate replacement by calcite. These grains are in optical continuity with the replacing material. There are also some grains that have not yet recrystallized scattered throughout the vein.

The question arises as to the mechanism of cementation. The following two different mechanisms are suggested:

1.—Dissolution at points of high compressive stress and reprecipitation at points of low stress. For example, as long as the pore space is filled with water the grain to grain contact is limited; the existing pressures are, however, hydrostatic except at the points of grain to grain contacts. The pores begin to fill gradually with precipitated calcite, giving rise to cement. As the process proceeds, the pressure becomes geostatic. Later, as the thickness of sediments increases, solution of pre-existing grains at points of high compressive stress will take place.

TABLE 1.—*Spectrographic Analyses of the four samples of Salem Limestone*

	1	2	3	4
Mgo	0.40%	0.45%	0.80%	0.40%
Fe	0.09	0.06	0.05	0.01
Al_2O_3	0.09	0.12	0.03	0.02
MnO	0.01	0.006	0.005	0.006
SiO_2	0.85	0.70	0.16	0.12
SrO	0.02	0.015	0.02	0.01

2.—Dissolution of the organically formed calcite because it is unstable for reasons different from stress, namely because there is an unstable amount of MgO present as impurities in the organic calcite; therefore, reprecipitation of stable calcite in pores will occur.

The newly precipitated cement is nearer to the thermodynamic state of equilibrium than the organically precipitated, metastable calcite of the fossils. The result is a further growth of cement-like calcite in preference to the pre-existing organically precipitated crystals.

In general, the cementation and consolidation of limestone will follow somewhat similar paths. The hydrostatic pressure is dependent upon the depth of the overburden. The solubility of limestone is greater at higher pressures than at lower pressures (lesser depths). The $Ca^{++}CO_3^{--}$ in solution will migrate to the areas of lesser pressure (lesser depths) where it will precipitate, fill the pores, and cement the sediments. The process of cementation will thus proceed upward and will be generally accelerated since the pressure will be more geostatic in character.

REFERENCES

CHAVE, K. E., 1954, Aspects of the biogeochemistry of magnesium. 2. Calcareous sediments and rocks: Jour. Geology, v. 62, p. 587–599.

GOLDSMITH, J. R., GRAF, D. L., AND JOENSUU, O. I., 1955. The occurrence of magnesian calcites in nature: Geochim. et Cosmochim. Acta, v. 7, p. 212–230.

REMOVAL OF HEAVY LIQUID SEPARATES FROM GLASS CENTRIFUGE TUBES—ALTERNATE METHOD[1]

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Fessenden (1959) described a method for and the benefits of freezing bromoform with dry ice to obtain clean separation of light and heavy minerals. In our laboratories we have found that in some cases liquid nitrogen yeilds better results than dry ice. This is particularly true for graded separations in the 2.5–2.8 sp g range, for heavy liquids other than bromoform, and very fine-grained material where the more rapid freezing reduces convection effects.

The liquid nitrogen is kept in a heavily taped pint thermos for daily operations. During the freezing operation the nitrogen, in small amounts, is poured into a 50 cc beaker. The end of each tube containing the separates is touched to the nitrogen for a few seconds. The amount of freezing is readily controlled. Ordinarily only the heavy liquid in the tapered part of the centrifuge tube is frozen.

Our PVT laboratory purchases liquid nitrogen in 15 liter lots from which we can draw a daily supply. We rarely use more than a liter a week for separations so the cost is minor—less than a dollar per week. The 15 liter containers, if needed, represent an investment of approximately $150.00.

[1] Manuscript received March 4, 1960.

REFERENCE

FESSENDEN, F. W., 1959, Removal of heavy mineral separates from glass centrifuge tubes: Jour. Sedimentary Petrology, v. 29, p. 621.

ANNOUNCEMENTS

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RESULTS OF ELECTION OF OFFICERS OF THE SOCIETY OF ECONOMIC PALEONTOLOGISTS AND MINERALOGISTS FOR THE YEAR 1961–1962

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DISCUSSION

THE TERM GRAYWACKE[1]

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Professor Boswell's note in this *Journal* deploring the loose and varied use of the term "graywacke" is most timely. If the term is to be useful, its meaning must be reasonably definite and restricted. The term, as Professor Boswell notes, is an old one and one which has been difficult to define and one about which there has been much misunderstanding.

Graywackes are petrographically complex rocks and it is not easy to frame a simple, easily-applied, short definition for such rocks. Although definitions are in the last analysis matters of agreement, they should not disregard or ignore the original or type material. Fortunately there are two recent studies of the graywackes in the Harz Mountains where the term graywacke seems to have been first applied 120 years ago. The paper on the Tanner graywacke by R. Helmbold (1952) has been made generally known to American readers by reason of F. B. Van Houten's translation which appeared in the *Bulletin* of the Geological Society of America (Helmbold and Van Houten, 1958). More recently Bernhard Mattiat (1960) has published a similar paper on the Kulm graywackes also from the Harz. It is of interest to compare Mattiat's conclusions with the formal definitions of graywacke which have been made in recent years (Williams, Turner and Gilbert, 1954, p. 297; Folk, 1954, 1956; Pettijohn, 1957, p. 301; Fuchtbauer, 1959; Carozzi, 1960, p. 67; Crook, 1960). Mattiat's conclusion (freely translated) is: "I have regarded it as my task to give, as far as possible, a true description and characterization of the rock to which the name graywacke was first applied. This rock should once more be characterized as a graywacke, on the average consisting of 27 percent quartz; 19 percent feldspar, 21 percent interstitial material (chiefly chlorite and mica), 30 percent rock fragments, 2 percent heavy minerals, 1 percent other infrequent constituents."

We now have two well-documented studies of the original or "classical" graywackes. These should serve as petrological benchmarks and provide a sound basis for definition of the term graywacke.

[1] Manuscript received September 28, 1960.

REFERENCES

CAROZZI, A. V., 1960, Microscopic sedimentary petrography. New York, Wiley, 485 p.
CROOK, KEITH A. W., 1960, Classification of arenites: Am. Jour. Sci., v. 258, p. 419–428.
FOLK, R. L., 1954, The distinction between grain size and mineral composition: Jour. Geology, v. 62, p. 344–359.
———, 1956, The role of texture and composition in sandstone classification: Jour. Sedimentary Petrology, v. 26, p. 166–171.
FUCHTBAUER, HANS, 1959, Zur Nomenklatur der Sedimentgesteine: Erdöl und Kohle, v. 12, p. 506–613
HELMBOLD, R., 1952, Beitrag zur Petrographie der Tanner Grauwacke: Heidelbg. Beitr. Mineral. u. Petrogr., v. 3, p. 243–288.
HELMBOLD, R., AND VAN HOUTEN, F. B., 1958, Contribution to the petrography of the Tanner graywacke: Geol. Soc. America Bull., v. 69, p. 301–314.
MATTIAT, B., 1960, Beitrag zur Petrographie der Oberharzer Kulmgrauwacke: Beiträge z. Min. u. Petrogr., v. 7, p. 242–280.
PETTIJOHN, F. J., 1957, Sedimentary rocks. New York, Harper, 718 p.
WILLIAMS, H., TURNER, F. J., AND GILBERT, C. M., 1954, Petrography. San Francisco, Freeman, 406 p.

UPPER CARBONIFEROUS SEDIMENTATION IN DERBYSHIRE[1]

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Allen (1960) has evolved an interesting concept concerning the mode of deposition of the Mam Tor Sandstones in Derbyshire, and it is worth recording that a similar pattern of sedimentation, although with significant differences, is present at higher Namurian horizons within the same general area. In 1952 detailed work commenced on the lithology of sediments derived from a series of borings put down through upper Namurian and lower Westphalian rocks a few miles to the east of the main outcrop of the Mam Tor Sandstones (Greensmith, 1955). Throughout the cumulative vertical succession of 1000 ft or so of strata examined, sole structures similar to those of Allen's were found at the base of some of the sandier and siltier layers, and a large proportion of the siltier layers showed structures of the slump-ball type. Some of the main horizons exhibiting these structures have already been recorded (Greensmith, 1956) as have the textural features of the sandstones many of which are poorly sorted and tend towards subgreywackes (Greensmith, 1957).

The essential difference, however, at these higher stratigraphical levels is the general absence of a sharp lithological break between the shales and the immediately overlying sandstone. In fact, Allen's gradational sequence (1960, p. 201) would have to be modified so as to read—(1) non-laminated sandstone, (2) laminated sandstone, (3) laminated siltstone, (4) silty shale, (5) shale, (6) silty shale, grading upwards into (7) laminated siltstone and, eventually, into non-laminated sandstone once again. In other words, a lithological rhythm is still present within the sediments although one not quite so precisely defined.

Only at one horizon, the Longshaw Grit, is there any indication of grading in Allen's sense with a relatively sharp basal sandstone "cut-off," and in this instance it was very tentatively suggested that turbidity currents may have played some part in sedimentation (Greensmith, 1955, p. 68–69).

Even though Allen's picture of early Namurian events in Derbyshire involves turbidity current type sedimentation, it is doubtful, therefore, if his inferences have equal validity for most of the later Namurian or earlier Westphalian sediments in the same area. This is notwithstanding the gross similarities in the nature of those sediments. Instead a relatively gentler intermittent deposit of coarser clastic material appears to have occurred.

Finally, it is pertinent to record that foreset bed readings taken by Miss P. Holmes at Ashover, 20 miles to the southeast, from sandstones approximately equivalent to and slightly younger in age than the Mam Tor Sandstones indicate a predominant southwest dipping depositional slope to the area of sedimentation.

[1] Manuscript received August 11, 1960.

REFERENCES

ALLEN, J. R. L., 1960, The Mam Tor Sandstones: a "turbidite" facies of the Namurian deltas of Derbyshire, England: Jour. Sedimentary Petrology, v. 30, p. 193–208.

GREENSMITH, J. T., 1955, A study of some Upper Carboniferous sediments with particular reference to the mode and environment of sedimentation: Sheffield Univ. Ph.D. thesis. 178 p.

———, 1956, Sedimentary structures in the Upper Carboniferous of north and central Derbyshire, England: Jour. Sedimentary Petrology, v. 26, p. 343–355.

———, 1957, Lithology, with particular reference to cementation, of Upper Carboniferous sandstones in northern Derbyshire, England: Jour. Sedimentary Petrology, v. 27, p. 405–416.

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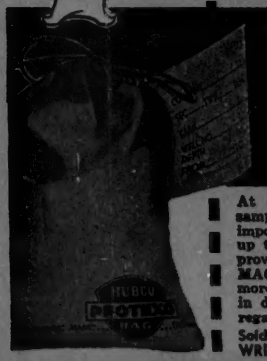

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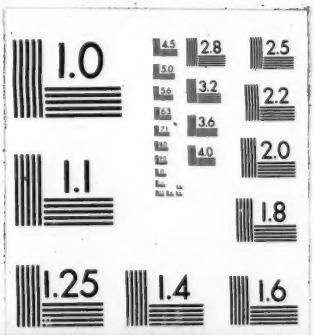
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